The polarization reverse of diode-like conical nanopore under pH gradient

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Abstract

In the past decade, with the improvement of nanofabrication technology, silica nanopores and nanochannels have been widely used in the fields of ion pumps, energy conversion, ion channels, metal ion detection, and biosensors. Although both potential and pH gradient can significantly change the performance of ion current rectification in nanoscale, the potential mechanism is still not fully understood. In this study, the ion current rectification, surface charge distribution and ion selectivity of silica nanopore under different background salt concentration and pH gradient were discussed by an analytical model, which takes into account the effects of electroosmotic flow, multiple ionic species, and the acid base neutralization. The results show that the polarity of nanopore rectifier can be changed by changing the acidity and alkalinity at both ends of the nanopore. For the first time, we find that the rectification polarity of silica conical nanopore exhibits different performances under high and low electric field intensity. One case in this study shows the rectification ratio curve of the nanopore will have a maximum or minimum value and the extreme point is near the zero of the ion current. With the increase of the concentration of background salt solution, the voltage at the zero point of ion current approaches the zero point, and then the maximum or minimum point moves to the left. The extreme point offset and polarity reversal phenomena may have potential application value in nanopore-based sensing devices.

Keywords Nanopore · Nanofluidics · pH · Surface charge density

1 Introduction

Since the discovery of ion current rectification (ICR) in nanopipette, the nonlinear I-V characteristics of nanopore and nanochannel have attracted much attention of the researchers [1–3]. The main carriers for studying ICR phenomena at the nanoscale are biological nanopore and solid nanopore [4, 5]. Among them, silica nanopore has the advantages of easy fabrication and processing. This advantage provides great convenience for the study of ion transport, chemical reaction and ion current rectification at the nanoscale. Besides, silica nanopores and nanochannels are widely used in ion pumps, energy conversion [6–10], ion

channels [11–13], metal ion detection [14–16], and biosensors [17–19]. In previous numerical simulation studies, the effects of ion species [20, 21] and ion concentration [22, 23] in background salt solution on nanopore and nanochannel have been deeply discussed in the study. However, pH has important effects on ion transport, surface chemical reaction equilibrium, and ion screening [24–26], we need to understand the internal mechanism.

Recent studies have added the influence of pH spatial distribution [27–29] to the model on ion transport, ion selection and surface chemical reaction balance of conical nanopore [30, 31]. In conical nanopores, the inhomogeneous surface charge distribution and ion depletion/

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accumulation [32, 25] caused by the asymmetric geometry [33] are considered to be the causes of ICR in conical nanopores. The results show that under the same electric field direction, different pH spatial distribution will affect the ion selectivity of the conical nanopore. That is to say, under the same electric field, the ion depletion/accumulation state of the conical nanopore will change [34].

In previous studies, the effects of background salt species, background salt concentration and geometry of nanopores or nanochannel on ion selection, ion transport and ion rectification were studied. As we know, the silica conical nanopore has advantages on easy processing and manufacturing and pH distribution has a great influence on ion transport and surface charge regulation [35]. In this study, the silica conical nanopore is used as research carrier to get a deep understanding of the influences of pH distribution on ion current rectification and surface charge regulation [36]. The effects of different background salt concentration, electric field and pH gradient on ion selection, ion transport and ion rectification of silica nanopore on ICR are studied by numerical simulation. Due to the consideration of acid-base neutralization reaction, surface chemical reaction [37, 38], and electroosmotic flow [39, 40] in this model, the simulation results are close to the real situation. In this paper, firstly we developed an analytical model which has been verified, and we proposed a detailed explanation of ion current rectification under a variety of pH gradients. The research results provide guiding significance for the fabrication of silica nanopores, and have potential application value in the direction of logic nanofluidic devices.

2 Mathematical model

We consider a nanostructure which consists of two reservoirs connected by a conical nanopore with axial length L , tip radius R_t , and base radius R_b . As illustrated in Fig. 1, the nanopore connects a fluid reservoir on either end and it is filled with the fluid made of background salt KCl, whose

pH is adjusted by KOH and HCl. The fluid is incompressible Newtonian fluid with density ρ , dynamical viscosity μ , and permittivity ϵ . The radius and length of each reservoir are, respectively, b and L_R . In contrast to the existing studies, an axial pH gradient is imposed by adjusting the pH values of the fluids in the two reservoirs. The charged walls (segment DE, CD and EF in Fig. 1) bear a surface charge (σ) which is regulated by the local pH nearby the walls. Note that the surface charge density is spatially dependent, which is different from the existing hypothesis of constant surface charge density adopted in the studies. Under the condition of a relatively large reservoir, the bulk ionic concentration and pH remain constant at AB and GH. Counterions accumulate next to the charged surface and the electric double layer (EDL) is formed. The electric field is generated by applying a potential difference between each end of the reservoirs (segment AB and GH). The cylindrical coordinate system (r, z) is used because of the axisymmetric geometry. The origin is located at the mid-point of AH. The axial z coordinate is parallel to AH and the radial r coordinate is parallel to AB.

A large number of researchers have used continuum model and molecular dynamic (MD) [41] to investigate the ion current rectification in nanoscale. Considered that the time scale limitation (100 ns) and much higher applied voltage of MD methods, herein, we employ continuum model to handle nanopore model.

The inertial term is neglected due to the extremely low Reynolds number:

$$-\nabla p + \mu \nabla^2 \mathbf{u} - F \sum_{i=1}^4 z_i c_i \nabla \phi = 0 \quad (1)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (2)$$

In the above equations, μ is the fluid viscosity, $\mathbf{u}$ represents fluid velocity. The bold letter represents vector; p represents pressure; ϕ represents the electric potential; c_1, c_2, c_3 and c_4 represent the molar concentration of K^+, Cl^-, H^+ and OH^- in the solution; z_1, z_2, z_3 and z_4 represent

Fig. 1 The schematic diagram of nanostructure which consists of two reservoirs connected by a conical nanopore. The surface charge density of charged surface (segment CD, DE, and EF) becomes spatially dependent under an axial pH gradient. An electroosmotic flow and ionic current are generated subject to an imposed axial electric field

the valence of K^+ , Cl^- , H^+ and OH^- ; F represents Faraday constant.

For the existing of stern layer, the velocity of fluid at the charged wall is zero ($u_{w1}=0$). A nonslip condition is imposed on the wall of the conical nanopore and a part of the surface of reservoirs (segments CD, DE, and EF). The segment AH is the axis of symmetry, so axisymmetric boundary condition is applied. The slip boundary condition is imposed on these uncharged walls of reservoirs (segment BC and FG). The slip boundary condition prescribes a no-penetration condition, $\mathbf{u} \cdot \mathbf{n} = 0$, it is implicitly assumed that there are no viscous effects at the slip wall and hence, no boundary layer develops. Besides, the open boundaries, on which fluid can get into and out, are set on the upper and lower edges of the two reservoirs, segment AB and GH ($p=0$), which describes how the boundaries contact with the large quantity of fluid. The initial speed of fluid is 0 m/s.

The flux density for each ionic species consists of convection, diffusion, and electromigration:

$$\mathbf{N}_i = \mathbf{u}c_i - D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \phi \quad (i = 1, 2, 3 \text{ and } 4) \quad (3)$$

In the above, the diffusion coefficient of i th ionic species is described by D_i , the absolute temperature of the solution is described by T , and R represents universal gas constant.

The Nernst-Planck (NP) equation is used to describe the concentration of each ion under the steady condition:

$$\nabla \cdot \mathbf{N}_i = 0 \quad (i = 1, \dots, 4) \quad (4)$$

The link between the concentration of each ion and potential is described by the Poisson equation, ϵ_f is the fluid permittivity:

$$-\epsilon_f \nabla^2 \phi = F \sum_{i=1}^4 z_i c_i \quad (5)$$

The charged and uncharged walls are impervious to ions. Hence, the ionic flux in the normal direction is zero:

$$\mathbf{n} \cdot \mathbf{N}_i = 0 \quad (6)$$

The $\mathbf{n}$ represents the local unit normal vector of the impervious walls. Due to the relatively large reservoir, zero normal flux is also imposed on the segments BC and FG. On AB and GH, the background salt of the solution is KCl , the bulk concentration is C_{KCl} . Due to electric neutrality, concentrations of H^+ , K^+ , Cl^- and OH^- are (unit: mol/m³):

$$C_1 = 10^{-pH+3} \quad \text{and} \quad C_4 = 10^{-(14-pH)+3} \quad (7)$$

$$C_2 = C_{KCl} \quad \text{and} \quad C_3 = C_{KCl} + C_1 - C_4 \quad \text{when } pH \leq 7 \quad (8)$$

$$C_2 = C_{KCl} + C_1 - C_4 \quad \text{and} \quad C_3 = C_{KCl} \quad \text{when } pH > 7 \quad (9)$$

The axisymmetric boundary condition is imposed on the axis of the nanopore for both the ionic concentration of each species and electric potential. The electric potential (V) is imposed on AB. GH is linked to the ground:

$$\phi\left(r, -\left(L_R + \frac{L}{2}\right)\right) - V = \phi\left(r, \left(L_R + \frac{L}{2}\right)\right) = 0 \quad (10)$$

The uncharged surface (segments BC and FG) is controlled by:

$$\mathbf{n} \cdot \nabla \phi = 0 \quad (11)$$

Surface charge density of charged wall (segments CD, DE, and EF):

$$\mathbf{n} \cdot (-\epsilon_f \nabla \phi) = \sigma \quad (12)$$

The surface charge density is spatially dependent, and is determined by the surface chemical reactions:

For the constant surface density of the ionizable sites:

$$\Gamma^{(0)} = \Gamma_{SiOH} + \Gamma_{SiO^-} + \Gamma_{SiOH_2^+} \quad (15)$$

The equilibrium constant K_A and K_B are described by:

$$K_A = \frac{\Gamma_{SiO^-} c_{H^+}^{(0)}}{\Gamma_{SiOH}}, \quad K_B = \frac{\Gamma_{SiOH} c_{H^+}^{(0)}}{\Gamma_{SiOH_2^+}} \quad (16)$$

The local surface charge density could be described as

$$\sigma = -q\Gamma^{(0)} \left\{ \frac{K_A - K_B [c_{H^+}^{(0)}]^2}{K_A + [c_{H^+}^{(0)}] + K_B [c_{H^+}^{(0)}]^2} \right\} \quad (17)$$

In the above, q represents units of the elementary charge; and $c_{H^+}^{(0)}$ is the concentration of H^+ at the wall/liq-uid interface. The induced ionic current is

$$I = F \int_S \sum_{i=1}^4 z_i \mathbf{N}_i \cdot \mathbf{n} dS \quad (18)$$

With S being the plane of either the anode or cathode due to the current conservation. Divide the magnitude of ion current when $V > 0$ by the magnitude of ion current when $V < 0$ with same $|V|$, then use the absolute value of consequence, we get the current rectification ratio (R_{ic}).

3 Results and discussion

The model described above is implemented numerically by COMSOL Multiphysics (version 5.2). The computational area is divided into triangle and rectangle elements. And there are at least 15 boundary layers in EDL. Extremely-fine mesh is also applied to the regions close to the charged wall. Element size parameters of extremely fine mesh are shown as below: Maximum element size is 3.35 nm; Minimum element size is 0.01 nm; Maximum element growth rate is 1.05; curvature factor is 0.2; resolution of narrow regions is 1. The tests of rigorous mesh-refinement are applied to guarantee that the consequence is mesh-independent and convergent. The magnitude of the elements in the computational area is over 3×10^5 to guarantee that the relative difference $|I_a - I_c|/|I_a|$ is at most 0.02% with I_a and I_c being ion current at the anode and cathode, respectively. The parameters considered in this study are shown as follows: $T = 300\text{K}$, $D(K^+) = 1.95 \times 10^{-9}\text{m}^2/\text{s}$, $D(Cl^-) = 2.03 \times 10^{-9}\text{m}^2/\text{s}$, $D(H^+) = 9.31 \times 10^{-9}\text{m}^2/\text{s}$, $D(OH^-) = 5.3 \times 10^{-9}\text{m}^2/\text{s}$, $K_A = 10^{-7.6}$, $K_B = 10^{-1.9}$, $\Gamma_{(0)} = 8\text{ nm}^{-2}$, $\varepsilon_f = 7.08 \times 10^{-10}\text{ F/m}$, $\mu = 0.001\text{ Pa} \cdot \text{s}$. The dimensions of the geometry are $R_t = 5\text{ nm}$, $R_b = 130\text{ nm}$, $L = 200\text{ nm}$, $b = 500\text{ nm}$ and $L_R = 500\text{ nm}$. In this study, the ion current rectification phenomena under four background salt concentrations and pH gradients are discussed, and the reasons for the ion rectification phenomena are analyzed. The concentrations of four kinds of background salt solution are 10 mM (C_{10}), 40 mM (C_{20}), 70 mM (C_{30}), and 100 mM (C_{40}), respectively. The four pH gradients (pH_1 , pH_2 , pH_3 and pH_4) are: the left end is 4, the right is 10; the left end is 10, the right end is 4; the left end is 3, the right end is 11; the left end is 11, the right end is 3.

The applicability of our model is verified by fitting it to the experimental data of Petrossian et al. [42]. In Petrossian's experiment, the conductance for the case of a silica solid-state nanopore of $L_N = 360\text{ nm}$, $R_N = 60\text{ nm}$ and background solution pH of 8 at the potential bias $V = 100\text{ mV}$ was demonstrated. As shown in Fig. 2, our model successfully illustrates the experimental data.

3.1 I-V characteristics under different pH gradients and background salt concentrations

In this research, the I-V characteristic of the conical nanopore is explored under different pH gradients and background salt concentration. We find that the conical nanopore exhibits different non-linear I-V characteristics under different pH gradients and background salt concentration.

As shown in Fig. 3, the I-V curves for different pH gradients and background salt concentrations are obtained.

Fig. 2 Conductance of pH-regulated silica nanopore as a function of background salt concentration with length $L_N = 360\text{ nm}$. Solid line: present numerical result at $R_N = 60\text{ nm}$, $\text{p}K_A = 7$, $\text{p}K_B = 2$ and $\Gamma_{\text{Total}} = 4.8\text{ nm}^{-2}$; discrete symbols: experiment data of Petrossian et al. [42]

It can be seen from the figure that the conductivity of the nanopore varies significantly in the voltage range studied. Among them, the ionic currents of Fig. 3a, c have the same changing trend, while those of Fig. 3b, d have the same changing trend. Moreover, the conductivity of the nanopore in Fig. 3a, c decreases, and in Fig. 3b, d, the conductivity of the nanopore also increases. When the voltage is -0.5V , the absolute value of ion current in Fig. 3c is larger than that in Fig. 3a at the same background salt concentration. When the voltage is 0.5V and the concentration of background salt solution is 100 mM, the ion current in Fig. 3b is larger than that in Fig. 3d. When the concentration of background salt solution is 10 mM, 40 mM, and 70 mM, the ion current in Fig. 3b is less than that in Fig. 3d. In Fig. 3, it can be seen that the conductivity of nanopore increases with the increase of the concentration of background salt solution, and the ion current at high background salt concentration is larger than that at low background salt concentration at the same voltage. In Fig. 3a, the pH of the tip side of the nanopore is 4, and the pH of the base side is 10. In Fig. 3c, the pH of the tip side of the nanopore is 3 and the pH of the base side is 11. We know that the pH of the left end is respectively 4 and 3 in Fig. 3a, c and the pH of the right end is 10 and 11, respectively, in Fig. 3a, c. Under these conditions, hydrogen ion and hydroxyl ion have same move direction but different ionic flux, so we get similarity in changing trend of ion current with voltage in Fig. 3a, c. In the same way, Fig. 3b, d show similar changing trend of ion current.

Fig. 3 I-V characteristic curves of nanopore under four background salt concentrations and pH gradients. The pH distributions of the diagrams are: (a) the left end of the nanostructure is 4 (segment

AB) and the right end of the nanostructure (segment GH) is 10; (b) the left end is 10 and the right end is 4; (c) the left end is 3 and the right end is 11; (d) the left end is 11 and the right end is 3

As shown in Fig. 4, the absolute value of applied potential ranges from 0.1 V to 0.5 V. R_{ic} decreases with the increase of voltage in Fig. 4a, c. R_{ic} increases with the increase of voltage in Fig. 4b, d. Different pH gradients and background concentrations result in varying distribution of surface charge density and Debye length (typical range is from 1.2 nm to 3.05 nm), further leading to the fluctuating curves of R_{ic} .

3.2 ICR under different pH gradients and background salt concentrations

In the processing of calculation, these consequences show that the ion current is not zero when the voltage is 0 V for the pH gradient between the tip and base side of the conical nanopore. In this study, we mainly discuss the ion current rectification near zero.

Table 1 shows the magnitude of ion current under different pH gradients and background salt concentrations when the applied voltage is 0 V. The four pH gradients (pH_1 , pH_2 , pH_3 and pH_4) are: the left end is 4, the right is 10; the left end is 10, the right end is 4; the left end is 3, the right end is 11; the left end is 11, the right end is 3. From the table we know that the ion current is positive under pH_1 and pH_3 , and negative under pH_2 and pH_4 . Under pH_1 and pH_3 , hydrogen ions flow from tip side of the nanopore to base side of the nanopore, which makes the ion current positive. Under pH_2 and pH_4 , hydrogen ions flow from base side of the nanopore to the tip side of the nanopore, which makes the ion current negative. This table shows that ion current decreases with the increase of background salt concentration. This table would partly explain the reason for local maximum (minimum) point in Fig. 5 (Fig. 6).

Fig. 4 The ICR ratio, R_{ic} , as a function of the absolute value of potential (0.1 V–0.5 V) in different salt concentration of the bulk solution and different pH gradient. The pH distributions of the dia-

grams are: **(a)** the left end is 4 and the right end is 10; **(b)** the left end is 10 and the right end is 4; **(c)** the left end is 3 and the right end is 11; **(d)** the left end is 11 and the right end is 3

Table 1 ion current under different pH gradients and background salt concentrations when the voltage is 0 V (nA)

pH gradients	C_{10}	C_{20}	C_{30}	C_{40}
pH ₁	6.82×10^{-4}	6.72×10^{-4}	6.70×10^{-4}	6.69×10^{-4}
pH ₂	-6.96×10^{-4}	-6.85×10^{-4}	-6.82×10^{-4}	-6.81×10^{-4}
pH ₃	6.67×10^{-3}	6.66×10^{-3}	6.66×10^{-3}	6.66×10^{-3}
pH ₄	-6.81×10^{-3}	-6.78×10^{-3}	-6.78×10^{-3}	-6.78×10^{-3}

As shown in Fig. 5, in Fig. 5a, R_{ic} decreases with the increase of voltage, and when the background salt solution is 10 mM, the R_{ic} ranges from 5.3 to 1.1. With the increase of the concentration of background salt solution, the fluctuation of R_{ic} with voltage decreases, and when the concentration of background salt solution is 100 mM, R_{ic} tends to be 1. In Fig. 5b, R_{ic} increases with the increase

of voltage, and R_{ic} is less than 1. It shows that when the voltage is positive the ion current generated is less than that when the voltage is negative under pH₂. At the same time, when the background salt solution is 10 mM, the R_{ic} ranges from 0.19 to 0.86. R_{ic} decreases with the increase of background salt concentration. In Fig. 5c, it has a local maximum point for each curve when the background salt concentration is 10 mM and 40 mM. When the background salt concentration is 10 mM, the voltage at which R_{ic} takes the maximum value is greater than that of the background salt concentration at 40 mM. When the background salt concentration is 70 mM and 100 mM, R_{ic} decreases with the increase of voltage. In Fig. 5d, R_{ic} is also less than 1 under pH₄. It has a local minimum point for each curve when the background salt concentration is 10 mM and 40 mM. When the background salt concentration is 10 mM, the voltage at which R_{ic} takes the minimum value is greater than that of the background salt concentration at 40 mM.

Fig. 5 The ICR ratio, R_{ic} , as a function of the absolute value of potential in different salt concentration of the bulk solution and different pH gradient. The pH distributions of the diagrams are: (a) the

left end is 4 and the right end is 10; (b) the left end is 10 and the right end is 4; (c) the left end is 3 and the right end is 11; (d) the left end is 11 and the right end is 3

Fig. 6 The average velocity of z direction at the tip of nanopore as a function of voltage under different pH distribution when background salt concentration is 10 mM

R_{ic} increases with the increase of voltage when the concentration of background salt concentration is 70 mM and 100 mM.

Figure 5 shows that when the left end is acidic and the right end is alkaline, R_{ic} is greater than 1. When the left end is alkaline and the right is acidic, R_{ic} is less than 1. This phenomenon is like that the nanopore changes from a forward diode to a backward diode. Here we call it polarization reverse, that is, by changing the acidity and alkalinity of the tip and base side of the nanopore, the rectification polarity of the nanopore will be changed. As shown in Table 1, the ionic current generated by the pH gradient will also increase with the increase of the pH gradient. There is a condition that the direction of ion current generated by the pH gradient is opposite with the direction of ion current generated by electric field, so the ion current would tend to be zero under specific electric field. For Fig. 5c, because the ion current is positive when applied voltage is 0 V,

the direction of this specific electric field is from the base to the tip. For Fig. 5d, because the ion current is negative when applied voltage is 0 V, the direction of this specific electric field is from the tip to the base. As a result, it has a local maximum point for each curve when the background salt concentration is 10 mM and 40 mM in Fig. 5c, and a local minimum point for each curve when the background salt concentration is 10 mM and 40 mM in Fig. 5d. In Fig. 5c, d, when the concentration of background salt solution is 10 mM and 40 mM, the stationary point of the curve moves to the left with the increase of background salt concentration, because the influence of pH gradient on ion current is weakened with the increase of background salt concentration, and conductivity of nanopore increases with the increase of background salt concentration.

3.3 Distribution under different pH gradients and background salt concentrations

In order to get a deep understanding of the polarization reverse phenomenon and obtain the maximum or minimum point near the zero, we have further investigated the ion, surface charge density and pH spatial distribution under different background salt concentration, potential and pH distribution, and we have illustrated the average velocity of z direction at the tip of nanopore as a function of voltage under different pH distribution when background salt concentration is 10 mM.

As shown in Fig. 7, under the influence of electric field and pH gradient, the pH gradient distribution near the wall of the nanopore is generated. At the initial state, the hydrogen ion concentration at the tip side of the nanopore in Fig. 7c is 10 times the concentration of hydrogen ion at the tip side of the nanopore in Fig. 7a. The concentration

Fig. 7 The distribution of hydrogen ions near the wall of nanopore under four voltage and pH distributions when the concentration of background salt solution is 10 mM. The pH distributions of the dia-

grams are: **(a)** the left end is 4 and the right end is 10; **(b)** the left end is 10 and the right end is 4; **(c)** the left end is 3 and the right end is 11; **(d)** the left end is 11 and the right end is 3

Fig. 8 When the concentration of background salt solution is 10 mM, the surface charge density of nanopore under four voltages and pH gradients. The pH distributions of the diagrams are: (a) the

left end is 4 and the right end is 10; (b) the left end is 10 and the right end is 4; (c) the left end is 3 and the right end is 11; (d) the left end is 11 and the right end is 3

of hydroxyl ion at the base side of the nanopore at Fig. 7c is 10 times the concentration of hydroxyl ion at the base side of Fig. 7a nanopore. Therefore, although Fig. 8a, c have the same trend of surface charge density, the gradient of hydrogen ion spatial distribution in Fig. 7c is much larger than that in Fig. 7a. Similarly, for Fig. 8b, d, both have the same trend of surface charge density, but the gradient of hydrogen ion in Fig. 7d is much larger than that in Fig. 7b.

As shown in Fig. 7, when the voltage is negative, the difference of pH distribution on the nanopore wall is smaller than that on the nanopore wall when the voltage is positive. This is because when the voltage is negative, the electroosmotic flow flows from the base side of the nanopore to the tip side of the nanopore. When the voltage is positive, the electroosmotic flow flows from the tip side of the nanopore to the base side of the nanopore. Because of the influence of electroosmotic flow rectification, when the direction of electroosmotic flow is from the base side of nanopore to the tip side of the nanopore, the velocity of

electroosmotic flow is higher than that when the direction of electroosmotic flow is from the tip side of nanopore to the base side of the nanopore. The larger the electroosmotic flow velocity, the more bulk solution will flow into the conical nanopore, thus reducing the difference of pH distribution on the wall of the nanopore.

It can be obtained from Eq. (18) that the surface charge density of the nanopore wall is determined by the concentration of hydrogen ions near the pore wall. When the hydrogen ion concentration is large, the surface charge tends to be zero. When the hydroxide concentration near the nanopore wall is high, the surface charge density increases with the increase of hydroxyl ion concentration. Because the tip side of the nanopore in Fig. 8a, c is acidic, the surface charge density near the tip side tends to be zero. Similarly, due to the acidity of the base side of the nanopore in Fig. 8b, d, the surface charge density of the pore wall near the base side tends to be zero. As shown in Fig. 7, the concentration

of hydrogen ion in Fig. 7c at the same wall position is higher than that in Fig. 7a, so that the surface charge density in Fig. 8c at the same wall position is smaller than that in Fig. 8a at the same wall position. Similarly, the surface charge density at the same wall position in Fig. 8d is less than that at the same wall position in Fig. 8b.

Figure 9 shows the distribution of anions and cations near the pore wall under four pH gradients at voltages of -0.01 V and -0.1 V. As shown in Fig. 9, under the same conditions, the concentration of cations near the pore wall is always higher than that of anions near the pore wall. Compared Fig. 9a–c, when the voltage is -0.1 V, the pH of the tip side of the nanopore is 4, and that of the base side is 10, the adsorption of cations by the nanopore is stronger than that by the tip side of the nanopore at pH 3 and that by the base side at pH 11. From Fig. 9a, c, it is known that when the left end is acidic and the right end is alkaline, the

adsorption of cations by the nanopore wall is stronger at the voltage of -0.1 V than at the voltage of -0.01 V.

As shown in Fig. 8, the surface of the nanopore wall is always negatively charged, so the nanopore keeps electrostatic attraction to cations and electrostatic repulsion to anions. Therefore, the concentration of cations is always higher than that of anions at the same wall position in Fig. 9. Figure 8a shows that the surface charge density at the same wall position at the voltage of -0.1 V is greater than that at the same wall position at the voltage of -0.01 V. Because higher surface charge density attracts more cations, the cation concentration at -0.1 V is higher than that at -0.01 V in Fig. 9a. Similarly, in Fig. 9c, the cationic concentration at -0.1 V is higher than that at -0.01 V. Figure 8b shows that the surface charge density at the same wall position at the voltage of -0.01 V is greater than that at the same wall position at the voltage of -0.1 V. Therefore, in Fig. 9b, the cation concentration

Fig. 9 When the concentration of background salt solution is 10 mM and the voltage is -0.01 V and -0.1 V, the anions and cations distribution on the nanopore wall. The pH distributions of the

diagrams are: (a) the left end is 4 and the right end is 10; (b) the left end is 10 and the right end is 4; (c) the left end is 3 and the right end is 11; (d) the left end is 11 and the right end is 3

near the pore wall at the voltage of -0.01 V is higher than that at the voltage of -0.1 V. Similarly, in Fig. 9d, the concentration of cations near the pore wall at -0.01 V is higher than that at -0.1 V voltage. Compared with Fig. 8a, c, when the voltage is -0.1 V, the surface charge density in Fig. 8c is less than that in Fig. 8a. Therefore, in Fig. 9a, when the voltage is -0.1 V, the cation concentration is greater than that in Fig. 9c when the voltage is -0.1 V. At this time, the aggregation of cations by nanopore in Fig. 9a is greater than that by nanopore in Fig. 9c. According to Fig. 8b, d, when the pH of the left end is 10, the right end is 4, and the left end is 11, the right end is 3, and the voltage is -0.01 V and -0.1 V, the difference of surface charge density is small and tends to zero, so the adsorption ability of the nanopore wall to cations is low. Therefore, in Fig. 9b, d, when the voltage is -0.01 V and -0.1 V, the cation concentration tends to the body solution concentration.

Figure 10 shows the distribution of anion and cation concentration near the pore wall under four pH gradients at voltages of 0.01 V and 0.1 V. As illustrated in Fig. 10, under the same conditions, the concentration of cations near the pore wall is also always higher than that of anions near the pore wall. Compared with Fig. 10a, c, when the voltage is 0.01 V, the adsorption of cations by the nanopore is stronger under pH_1 than that under pH_3 . From Fig. 10a, c, it is known that when the left end is acidic and the right end is alkaline, the adsorption of cations by the nanopore wall is stronger under 0.01 V than that under 0.1 V.

Due to the negative surface charge, the wall of the nanopore keeps its attraction to cations and electrostatic repulsion to anions. Therefore, the concentration of cations is always higher than that of anions at the same wall position in Fig. 10 too. Figure 8a, c show that the surface

Fig. 10 When the concentration of background salt solution is 10 mM and the voltage is 0.01 V and 0.1 V, the anions and cations distribution on the nanopore wall. The pH distributions of the dia-

grams are: (a) the left end is 4 and the right end is 10; (b) the left end is 10 and the right end is 4; (c) the left end is 3 and the right end is 11; (d) the left end is 11 and the right end is 3

charge density at the voltage of 0.01 V is higher than that at the voltage of 0.1 V under pH_1 and pH_3 . Therefore, in Fig. 10a, c, when the voltage is 0.01 V, the cationic concentration is greater than that at 0.1 V. According to Fig. 8b, d, the surface charge density is different at 0.01 V and 0.1 V, and the surface charge density under 0.1 V is

higher than that under 0.01 V. Therefore, in Fig. 10b, d, the cation concentration near the nanopore wall at 0.1 V is higher than that near the nanopore wall at 0.01 V.

Figure 11 shows the pH distribution in the nanopore at different pH gradients and voltage (± 0.1 V). When the electric field is directed from right to left, the acidic or

Fig. 11 The distribution of pH in the nanopore is under two pH gradients, voltage (± 0.1 V), when the concentration of background salt solution is 10 mM. The pH distributions of the diagrams are: (a, b) the left end is 4 and the right end is 10; (c, d) the left end is 10 and

the right end is 4; (e, f) the left end is 3 and the right end is 11; (g, h) the left end is 11 and the right end is 3. Voltage in (a, c, e, g) is -0.1 V, in (b, d, f, h) is 0.1 V

alkaline solution outside the base side of the nanopore flows into the nanopore driven by electroosmotic flow. Similarly, when the electric field is directed from left to right, the acidic or alkaline solution outside the tip side of the nanopore flows into the nanopore driven by the electroosmotic flow. Due to the influence of electroosmotic flow rectification, the electroosmotic flow velocity from the base side of nanopore to the tip side of the nanopore is higher than that from the tip side of nanopore to the base side of nanopore under the same electric field intensity and different electric field directions. Therefore, the acidic or alkaline solution outside the base side of the nanopore enters into the nanopore more easily, thus presenting the pH distribution as shown in Fig. 11.

4 Conclusions

Taking acid-base neutralization, surface charge regulation, and electroosmotic flow into account, we develop a simple and general mathematical model to analyze the influence of pH gradient, voltage and salt concentration of the bulk solution on the rectification ratio of this structure which consists of conical nanopore and reservoirs. The current rectification ratio could be modified by the background salt concentration and pH gradient, which would provide a much convenient method to change the rectification ratio. The results also show that there will be a certain ionic current when the voltage is zero because of the pH gradient. Similarly, the voltage is not zero when current is zero. Furthermore, the consequences show that the rectification polarity of nanopore can be changed by changing the acidity and alkalinity at both ends of the nanopore. The rectification ratio curve of the nanopore will have a maximum or minimum value and the extreme point is near the zero of the ion current under pH_3 and pH_4 when the concentration of the background salt solution is 10 mM and 40 mM. With the increase of the concentration of background salt solution, the voltage at the zero point of ion current approaches the zero point, and then the maximum or minimum point moves to the left. The R_{ic} of the nanopore near the voltage zero point is more than 1 under pH_1 and pH_3 . The R_{ic} of the nanopore near the voltage zero is less than 1 under pH_2 and pH_4 . With the increase of electric field intensity, the R_{ic} of nanopore will decrease from more than 1 to less than 1 under pH_1 and pH_3 . R_{ic} will increase from less than 1 to more than 1 with the increase of electric field strength under pH_2 and pH_4 . This method of adjusting the rectification ratio and polarity through the pH at both ends of the nanopore and the concentration of background salt solution provides some guidance for the design of new logic nanofluidic devices,

which presents a certain potential application in the field of new nanofluidic devices.

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Compliance with ethical standards

Conflict of interest The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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