Surface charge density of the track-etched nanopores in polyethylene terephthalate foils

Jianming Xue,^{a)} Yanbo Xie, Yu Yan, Jin Ke, and Yugang Wang
State Key Laboratory of Nuclear Physics and Technology, Center for Applied Physics and Technology, School of Physics, Peking University, Beijing 100871, People's Republic of China

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Surface charge is one of the most important properties of nanopores, which determines the nanopore performance in many practical applications. We report the surface charge densities of track-etched nanopores, which were obtained by measuring the streaming current and pore conductance, respectively. Experimental results reveal that surface charge densities depend significantly on the salt concentrations. In addition the values obtained with the pore conductance were always several times higher than those calculated with the streaming current, and the gel-like surface layer on the nanopore was considered to be responsible for this discrepancy. © 2009 American Institute of Physics. [DOI: [10.1063/1.3130988](https://doi.org/10.1063/1.3130988)]

I. INTRODUCTION

Track-etched nanopores are fabricated by etching the ion tracks inside organic foils,¹ and they gain more and more attention due to their applications in biosensor,^{2,3} DNA sequencing,^{4,5} mimicking the ion channel,^{6,7} and energy conversion.⁸ In all these applications, surface charge is crucially important, since it governs ion transport through the pores, especially when the salt concentration is low.

Very few results on the surface charge property have been known for the track-etched nanopore because of a lack of accurate experimental data. Déjardin *et al.*⁹ measured the streaming potential with multitrack foils in a 0.01M KCl solution, and their results indicated that the surface charge density was around -0.012 C/m^2 . However, with this value, it is impossible to explain the current rectification behavior of the conical track-etched nanopores^{10–13} where the surface charge density was around 0.1 m C/m^2 . In addition, the surface charge density was treated as a constant in solutions with different salt concentrations in the above-mentioned works; its dependence on salt concentration is not known yet. Systematical experimental investigation on the surface charge of track-etched nanopores is of great interest both in mechanism study and practical application.

In this paper, we present our work on the surface charge density (σ) of track-etched nanopores made from polyethylene terephthalate (PET) foils. Two sets of measurements were carried out to obtain the surface charge density. One was to measure the streaming current when the salt solution was driven through the nanopores by external pressure;^{14,16} another experiment was performed by measuring the pore conductance.^{15,16} We used single nanopores in our experiments rather than multitrack ones. This is because the uniformity of the multitrack pore shape is hardly controlled, while a single nanopore can help us gain accurate insights into the electric mechanism of surface charge of a nanopore.

^{a)} Author to whom correspondence should be addressed. Electronic mail: jmxue@pku.edu.cn. Tel.: 86-10-62758494. FAX: 86-10-62751875.

II. THEORETICAL METHODS

A pressure-driven flow through a cylindrical nanopore induces a flow of countercharges inside the surface electric double layer (EDL). Ionic current could then be produced, which is called streaming current (I_{str}). The streaming current could be calculated with the following equation:

$$I_{\text{str}} = \int_0^R 2\pi r u(r) [\rho_+(r) - \rho_-(r)] dr, \quad (1)$$

where $u(r)$ and $\rho(r)$ are the velocity distribution and ion concentration profile in the radial direction, respectively, R is the pore radius, and r is the local radius. The conductance of the nanopore also depends on the surface charges, and it can be described with the following equation:

$$G = \int_0^R 2\pi r \mu_i \rho_i(r) dr, \quad i = \text{K}^+ \quad \text{and} \quad \text{Cl}^-, \quad (2)$$

where μ_i is the mobility of ion K^+ or Cl^- .

Inside a cylindrical nanopore, whose length is much larger than its diameter, the entrance and existence effect could be neglected. Then Poiseuille's law can be used to describe the velocity profile with a no-slip boundary condition,¹⁷

$$u(r) = \frac{1}{4\eta} (R^2 - r^2) \frac{\Delta P}{L}, \quad (3)$$

where L is the pore length, ΔP is the applied pressure, and η is the viscosity of water ($\eta = 1.007 \times 10^{-3}$ Pa s). The ion distribution in the radial direction could be determined with the following equation:¹⁷

$$\rho_{\pm}(r) = \rho_o \exp \left[\mp \frac{e_o \phi(r)}{kT} \right], \quad (4)$$

where ρ_o is the density of cations and anions in the neutral electrolyte, respectively, e_o is the proton charge, k is the Boltzmann constant, and T is the absolute temperature. $\phi(r)$ is the dimensionless electrical potential (1 unit corresponds to RT/F), and it is governed by the Poisson–Boltzmann equation as follows:

$$\nabla^2 \phi(r) = \sinh[\phi(r)]/\lambda^2, \quad (5)$$

where λ (the Debye length that represents the EDL thickness) is defined as $\lambda = \epsilon RT/2C_o F^2$, F and T are the Faraday constant and temperature, and ϵ and R are the dielectric permittivity of electrolyte solution and universal gas constant. Suppose the inner surface of the nanopore is charged homogeneously; the boundary condition for the above equation could be given by Gauss's law, $\nabla \phi = F\sigma/\epsilon RT$, where σ is the charge density on the inner surface on the nanopore.

If the surface charge density is known, then streaming current and pore conductance can be determined. In reverse, if the streaming current and the pore conductance are known when a certain nanopore is immersed in electrolyte, then the surface charge density can also be calculated. In our calculation, the above equations were numerically solved with the infinite element method. Details of the calculation can be found in our previous work.¹⁸

III. EXPERIMENTAL DETAILS

Nanopores investigated here were prepared with 12 μm thick PET foils. The foil was first bombarded with a single U^{235} particle with energy of 11.4 MeV/ u to form a latent ion track. After being irradiated with UV rays for 1 h, the foil was immersed in a 5M NaOH solution at room temperature. Since the etching rate in the ion track region is much faster than that in the bulk

FIG. 1. Scheme illustration of the setup to measure the streaming current and I - V curves. The foil with a single pore was mounted between the two cells. Current was measured with Ag/AgCl electrodes and recorded directly by a patch clamp of Axon 200B.

material, a cylindrical pore with a radius in the nanometer scale can be fabricated in each foil. Details of the nanopore fabrication method can be found in previous works.^{19,20}

The radius (R) of the track-etched nanopore was determined by measuring the pore conductance (G) with Ag/AgCl electrodes in a 1M KCl solution.¹⁹ The effective radii R can be calculated with $G = \pi\kappa R^2/L$, where κ (11.6 S/m) is the specific conductivity of 1M KCl and L is the pore length. In general, R calculated with this method has an error of about 5%. Two samples with different radii were used in our experiment; their radii were 107 nm (sample A) and 61 nm (sample B).

The experimental setup for measuring the streaming current is schematically illustrated in Fig. 1. The foil with a single nanopore was mounted between the two cells and immersed in a potassium chloride solution buffered with phosphorate ($\text{pH}=7.2$). The left cell was airtight, and pressed nitrogen gas drove the solution through the nanopore. The streaming current (I_{str}) was recorded directly by a patch clamp (Axon 200B) operated in the whole cell model ($\beta=1$) with a 1 kHz low pass Bessel filter. In all the measurements, Ag/AgCl electrodes were used to connect the two cells.

Pore conductance G was measured with the same facility. First, I - V curves of the pores were recorded by scanning the external voltage from 100 to 100 mV with a step of 10 mV, and then G was obtained by linearly fitting the I - V curves.

IV. RESULTS AND DISCUSSION

Streaming current was found to depend linearly on the applied pressure, as shown in Fig. 2(a). This perfect linear relation indicates that the deformation of the track-etched nanopore can be neglected when the external pressure is lower than 1 bar, since any slight deformation of the nanopore will cause great change in the value of the streaming current. Hence, 1 bar pressure was used in all the following measurement. Figure 2(b) shows the measured streaming current I_{str} in solutions with KCl concentration (C_0) ranging from 10^{-2} to $10^{-5}M$. While diluting the electrolyte solution, I_{str} decreases continually, which means that the surface charge density drops down.

FIG. 2. (a) Streaming current responses shown linearly with external pressure. (b) Streaming current (I_{str}) as a function of KCl concentration (C_0) for these two groups of samples, which have different radii. (c) Pore conductance at different KCl concentrations, which were obtained by linearly fitting the I - V curves. In all the plots, the triangles indicate sample A ($R=107$ nm) and the circles indicate sample B ($R=61$ nm). The solid lines are the theoretical calculation results. Details can be found in the text.

FIG. 3. (a) Surface charge densities obtained with streaming current (open symbols) or pore conductance (filled symbols) for samples A ($R=107$ nm) and B ($R=61$ nm). (b) Ratio of the surface charge density values measured with the two methods: σ_0/σ_s . Lines in the figures are the fitting of the experimental data with exponential equations.

With the measured I_{str} data, as shown in Fig. 2(b), surface charge densities, noted as σ_s , had been calculated, as shown in Fig. 3(a). The surface charge density as a function of the salt concentration can be fitted with exponential functions, and the fitted lines are shown as the lines in Fig. 3(a). With these fitted results of surface charge density, the I_{str} and G for every sample had been calculated, and the results are shown as the lines in Fig. 2.

It has been reported that the conductance was nearly a constant at low salt concentrations in silica nanochannels.¹⁵ However, our results show that [Fig. 2(c)], when KCl concentration was changed from 10^{-2} to $10^{-5}M$, the conductance of the track-etched nanopore decreased gradually but not at a constant rate. This indicates that the surface charge property of the track-etched nanopore in PET foils might be different than that on a silica surface. With the measured conductance data, the surface charge densities as a function of the salt concentration were calculated, and the results are shown in Fig. 3(a). The surface charge density obtained with this method is noted as σ_0 in the following.

Both σ_0 and σ_s depend significantly on the salt concentration; they drop down gradually while C_0 decreases. This might be explained by the less dissociation of carboxyl in a diluted electrolyte solution (salt effect). The surface charge densities of sample A are similar to that of sample B at each given salt concentration.

It has been reported that the surface charge density depends on the nanopore diameter of

track-etched multinanopore samples; it increases from 2.1×10^{-3} to 8.6×10^{-3} C/m² when the nanopore radius increases from 20 to 200 nm.²¹ However, we did not find systematic dependence on the nanopore radius in our measurement when the radii were ranged from 60 to 150 nm.

At a concentration of 0.01M, σ_s was in the range from -0.02 to -0.01 C/m². This value is in agreement with that of -0.012 C/m² measured by Déjardin *et al.*⁹ with multitrack samples inside 0.01M KCl. However, σ_0 was much higher than σ_s ; it was around -0.09 C/m² when the nanopore was immersed in a 0.01M KCl solution. With this value, the theoretical prediction is in good agreement with the current rectification behaviors of PET conical nanopores.^{10–13} If the track-etched nanopores are used in a lower concentration environment, such as in mimicking, the ions' channels where the salt concentration is only on the order of $10^{-3}M$, the dependence of σ_0 on the salt concentration must be taken into consideration.

The discrepancy between σ_s and σ_0 was significant, as shown in Fig. 3(a). σ_0 was always several times higher than σ_s at a given salt concentration. This obvious discrepancy cannot be diminished by adjusting the parameters used in the calculations. For a better comparison, ratios of σ_0/σ_s were calculated, and the results are shown in Fig. 3(b). In general, σ_0/σ_s is around 10, and it is slightly higher at lower C_0 . This result reveals that for track-etched PET nanopores, the effective surface charge densities in different physical process are not the same.

This difference was commonly attributed to the presence of the so-called stagnant layer near the wall surface where the counterions are enriched, and the conductance of this layer is called the surface conductance. In this layer, water molecules are impeded when external pressure is applied, but the ion can transport through this layer under the electric field.²² However, molecular dynamics simulation shows that when the pressure drives the fluidic transportation nanopore, this stagnant layer does not exist.²³ In other words, the physical basis of this stagnant layer was not clear, and there must be some special structures on the nanopore surface. For the track-etched nanopores, the gel-like layer on the nanopore surface should be responsible for this discrepancy. In the etching process, lots of broken PET molecules formed a loosened layer on the pore wall surface. Some of these broken polymer molecules had charged dangling bonds, which are the source of surface charges on the track-etched nanopore.^{24,25} The structure of this gel-like layer is illustrated in Fig. 4.

In an aqueous solution, this layer combines with water molecules to form a gel-like layer. Ions in this layer do not contribute to the streaming current because this layer is hydrodynamically immobile.²⁶ Therefore, I_{str} was determined by the net ionic charges outside the gel-like layer. In other words, it depends on the effective charge density σ_s on the solution-surface layer interface, not on the total number of charged dangling bonds (σ_0). However, all these ions, both inside the gel-like layer and solution, can move under the electric field and make a contribution to the final ionic current. Therefore, σ_0 is equal to the sum of charged dangling bonds in a unit surface area. Obviously, σ_0 is larger than σ_s since many counterions stayed inside the gel-like layer so that some of the charge dangling bonds were neutralized.

The thickness of this gel-like layer (T) could be estimated by assuming all the charged dangling bonds are on the interface between the gel-like layer and the PET wall. If we define σ_{K^+} to be the surface density of K^+ inside the gel-like layer, then $\sigma_s = \sigma_0 + \sigma_{K^+}$ and

$$\sigma_{K^+} = \int_{R-T}^R [\rho_K(r) - \rho_{Cl}(r)] dr \bigg/ (2\pi R),$$

where T is the thickness of the gel-like layer. When the salt concentration is 0.01M KCl, $\sigma_0 = -0.09$ C/m². If $T = 2$ nm, then $\sigma_{K^+} = 0.08$ C/m², and $[\sigma_0/\sigma_s]$ will be 8.9, which is similar to the measured values. However, when the salt concentration was only $10^{-5}M$, the calculated value of σ_0/σ_s was around 3 if we assumed that T was still 2 nm. To be consistent with experimental results, as shown in Fig. 3(b), T should be increased with the salt concentration. This thickness-increasing behavior could be understood by the higher swelling ratio of the gel materials in lower salt concentration solutions.²⁷

FIG. 4. Illustration of the surface of the track-etched nanopore. A gel-like layer was formed with the dangling bonds; it is hydrodynamically immobile, but ions can pass through under the electric field.

The discrepancy of the surface charges must be paid attention to in practical applications of the track-etched nanopores. For example, the pore diameter of a single track-etched nanopore is always determined with the pore conductance in a 1M KCl solution,¹⁹ but the surface charge effect was considered in the calculation. Therefore, the real geometrical diameter of the pore should be smaller than the calculated values due to the effect of the surface gel-like layer.

V. CONCLUSION

In conclusion, we have measured the streaming current through single PET nanopores and the conductance of nanopores to study the influence of surface charge on a nanopore system. The measured results show that the surface charge densities decrease when salt concentration drops down. Besides, the surface charge density obtained from the pore conductance is always much higher than that from the streaming current measurement. This interesting phenomenon is due to the gel-like layer on the surface of the track-etched PET nanopores.

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