Scan-Rate-Dependent Current Rectification of Cone-Shaped Silica Nanopores in Quartz Nanopipettes

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Abstract: Here we report the voltammetric behavior of cone-shaped silica nanopores in quartz nanopipettes in aqueous solutions as a function of the scan rate, v. Current rectification behavior for silica nanopores with diameters in the range 4−25 nm was studied. The rectification behavior was found to be strongly dependent on the scan rate. At low scan rates (e.g., $v <$ 1 V/s), the rectification ratio was found to be at its maximum and relatively independent of v. At high scan rates (e.g., $v >$ 200 V/s), a nearly linear current−voltage response was obtained. In addition, the initial voltage was shown to play a critical role in the current−voltage response of cone-shaped nanopores at high scan rates. We explain this v-dependent current−voltage response by ionic redistribution in the vicinity of the nanopore mouth.

The nonlinear current−voltage (i−V) response of both biological and artificial nanopores has received considerable interest in the past decades[1−4] because of its importance in many areas, such as micro/nanofluidics[5] and protein biophysics. The nonlinear i−V response, or current rectification, has been generally assumed to originate from the asymmetric distribution of surface charges on the pore walls.[2b] There have been numerous reports in the recent literature concerning both the origin of current rectification of nanopores[1,2b,6−8] and the control of the ionic/molecular transport properties of nanopores by studying their rectification behavior.[5]

We have recently been interested in studying the voltammetric response of cone-shaped silica nanopores as a function of scan rate, v. As recently reported by White and Bund,[3] the current rectification behavior of a cone-shaped glass nanopore is mainly due to a change in the ionic conductivity in the vicinity of the pore mouth at varying bias voltages. We therefore believe that such a change in the ionic conductivity at the pore mouth should involve a process of dynamic reorganization of the ionic species at different bias voltages.

Normally, this reorganization process is fast and unnoticeable under conventional experimental conditions, such as measurements with discrete voltages or low voltage scan rates. Under these conditions, the i−V response of a cone-shaped nanopore shows the most significant rectification behavior, which is normally independent of v and the initial voltage. It can be described as a "steady-state" response. However, we have found that at very high scan rates (e.g., $v >$ 200 V/s), the i−V response of a cone-shaped silica nanopore starts to show a strong dependence on both the scan rate and the initial voltage. In fact, the resulting i−V response under such conditions shows considerable ohmic behavior. A clear transition from strong rectification behavior to a nearly ohmic response with increasing scan rate has been observed. Furthermore, we have found that the i−V response is strongly dependent on the initial bias voltage of the voltage scan. The overall slope of the nearly linear i−V response is close to the slope at the starting voltage

when the scan rate is above ∼200 V/s. These results strongly suggest that current rectification of a cone-shaped silica nanopore could originate from a dynamic ionic reorganization process in the vicinity of the pore orifice under the influence of a changing bias voltage.

Individual cone-shaped silica nanopores with diameters in the range 4−25 nm were prepared by a laser-pulling process.[9] Both the diameter and the half-cone angle can be approximately adjusted in the laser-pulling process. Depending on the pulling process, a silica nanopore can have a half-cone angle that is usually between 5 and 10°. The size of a cone-shaped silica nanopore was determined by measuring its ionic resistance in an electrolyte solution (e.g., 1 M KCl).[10] Figure SI1a in the Supporting Information shows a scanning electron microscopy (SEM) image of a typical silica nanopore prepared using a laser puller. Figure SI1b shows the i−V response of a 4.6 nm silica nanopore at $v =$ 10 mV/s in three different KCl solutions. The rectification factor, which is defined as the ratio of the current at −0.5 V to that at +0.5 V, was measured to be 4.9, 3.6, and 1.8, for the 10, 100, and 1000 mM KCl solutions, respectively. The smaller rectification factor in the 1 M KCl solution can be qualitatively explained by the absence of an overlap in the electrical double layer in the vicinity of the nanopore mouth due to the sufficiently high concentration of electrolyte.

In order to study the scan-rate-dependent voltammetric response of a cone-shaped silica nanopore, a triangle voltage waveform was applied across the nanopore using a pair of Ag/AgCl electrodes and a function generator. The nanopore pipet was filled with the same electrolyte solution as in the bulk. A voltage scan range of 2 V (from −1 to +1 V) was used in all cases. Representative i−V responses can be found in Figure SI2. It is important to mention that at high scan rates, the i−V response of a cone-shaped silica nanopore typically involves a large capacitance charging current that is mainly due to the system capacitance. This results in a capacitance charging current of ∼2.7 nA at a scan rate of 200 V/s, corresponding to a system capacitance, C_{sys}, of ∼13 pF. The measured ionic current sits on top of this capacitance current. When a scan is initiated or the scan direction is changed, this capacitance charging current increases rather quickly and reaches a steady state. In the case of Figure SI2, for example, it takes less than 0.5 ms for the capacitance charging current to reach the steady state, which corresponds to <100 mV on the voltage scan. In order to make better comparisons between different scan rates avoiding interference from the increasing charging current, all of the i−V responses have been plotted over a 1 V scan range (from −0.5 to +0.5 V).

Figure 1a−c shows the i−V responses between −0.5 and +0.5 V of a 10 nm silica nanopore in Tris buffer solution containing KCl at three different concentrations (10, 100, and 1000 mM, respectively). The concentration of buffer was kept at 1% of the KCl concentration in all solutions. The same voltage waveform (0 → +1 V → −1 V → 0 V) was applied in all cases. It is worth
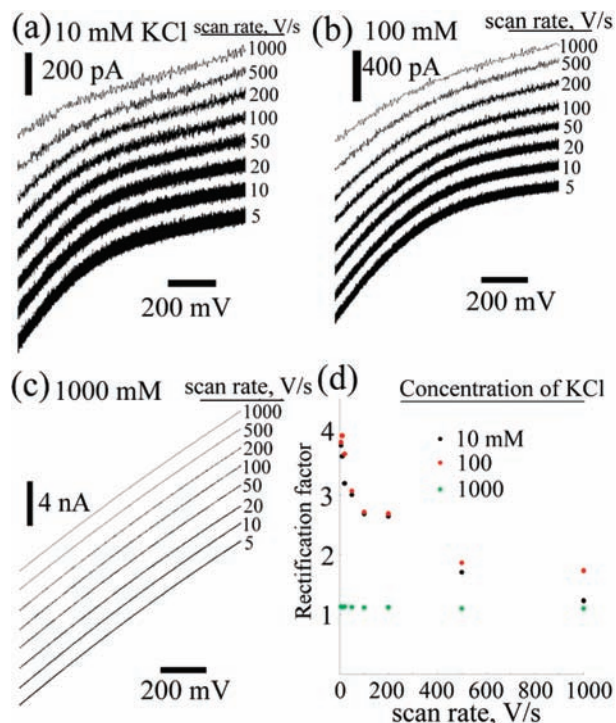
Figure 1. (a–c) Scan-rate-dependent $i-V$ responses of a 10 nm diameter silica nanopore in (a) 0.1 mM Tris buffer (pH 7.4) containing 10 mM KCl, (b) 1 mM Tris buffer (pH 7.4) containing 100 mM KCl, and (c) 10 mM Tris buffer (pH 7.4) containing 1000 mM KCl. (d) Rectification factors for (a–c) plotted as functions of the scan rate. The pore diameter was calculated from the conductance in 1 M KCl assuming a half-cone angle of 5°.

mentioning that no significant difference in the $i-V$ responses was observed for $v < 5$ V/s. Thus, only the scan rates between 5 and 1000 V/s have been displayed in Figure 1. At low scan rates, the nanopore showed the greatest current rectification effect. As v was increased, a clear transition from a strongly rectifying response to a nearly ohmic $i-V$ response was observed at 10 and 100 mM (Figure 1a,b). Interestingly, the rectification response of the same nanopore in the 100 mM KCl solution was found to be similar to that of the 10 mM solution. A similar transition was also observed in the 100 mM solution, as shown in Figure 1b. The nanopore showed a nearly linear $i-V$ response in 1 M KCl at all scan rates as a result of the smaller double-layer thickness ($\kappa^{-1} \approx 0.3$ nm[11]). Figure 1d summarizes the results shown in Figure 1a–c as a plot of the rectification factor as a function of v for the three KCl solutions. As shown in Figure 1d, the rectification factor decreased as the scan rate increased in the first two solutions. The decrease in the rectification factor was more obvious for the 10 mM KCl solution (from 3.8 to 1.2) than for the 100 mM solution (from 4.0 to 1.7). The rectification factor remained nearly constant at ~1.0 for the 1000 mM KCl solution, indicating nearly ohmic behavior.

More interestingly, the $i-V$ response of a silica nanopore was found to be strongly dependent on the initial voltage of the waveform at high scan rates. For example, Figure 2a,b shows the $i-V$ responses of a 10 nm silica nanopore in 10 mM KCl for two different voltage waveforms. A starting voltage of -0.8 V was used in Figure 2a, which shows that as v was increased, the overall $i-V$ response was nearly ohmic with a slope very close to that at -0.5 V. However, as shown in Figure 2b, when an initial voltage of $+0.8$ V was used, the overall $i-V$ response at high scan rates was also nearly linear but with a slope very close to that at $+0.5$ V. In fact, one can see that the effective conductance of the nanopore in Figure 2a was significantly higher than that in Figure 2b, although
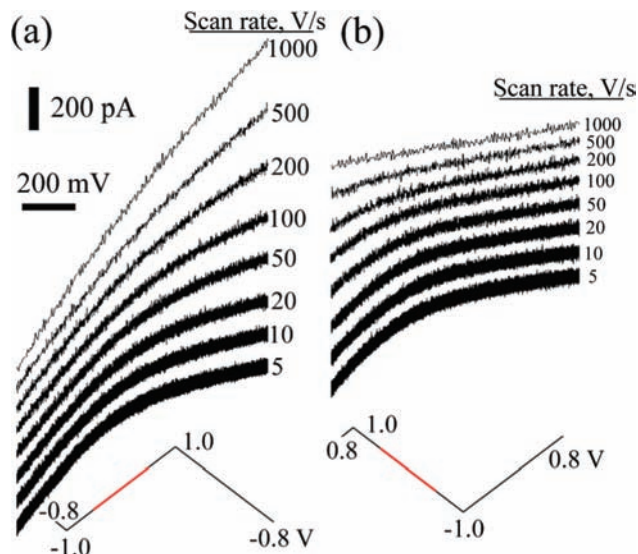
Figure 2. (a) Scan-rate-dependent $i-V$ responses of a 10 nm diameter silica nanopore in a 0.1 mM Tris buffer solution at pH 7.4 containing 10 mM KCl as the voltage is scanned starting from -0.8 V. (b) Scan-rate-dependent $i-V$ responses of the same nanopore in the same solution as the voltage is scanned starting from $+0.8$ V. The pore diameter was calculated from the conductance in 1 M KCl assuming a half-cone angle of 5°.

the only difference between the two conditions was a different starting voltage. We believe that at very high scan rates, the $i-V$ response of a charged conical nanopore is likely determined by the distribution of freely moving ions at the mouth of the nanopore *at the initial voltage*. Because the voltage perturbation is applied in an ultrashort time, the distribution of the freely moving ions may not have sufficient time to change, which would produce a nearly constant ionic resistance at all voltages in the scan (an ohmic response). A schematic has been given in Figure 3 to further explain the above two cases. When the voltage is scanned starting from a negative voltage, there should be fewer K^+ ions at the pore mouth, corresponding to a smaller ionic resistance. Therefore, a greater slope in the $i-V$ response would be expected, as illustrated in Figure 3 with the green curve. However, when the voltage scan starts from
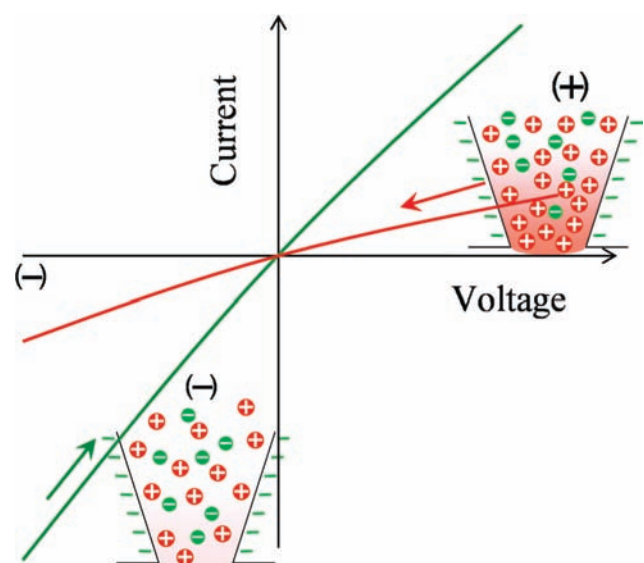

Figure 3. Schematic illustration of the $i-V$ responses at high scan rates when two different initial voltages are employed. Two different possible ionic distributions are shown to help explain the difference in ionic resistance.

a positive value, where the density of K^+ is at its maximum over the entire scan, a smaller slope should be obtained in the $i-V$ curve because of a greater ionic resistance, as depicted with the red curve in Figure 3. Such nearly linear responses, however, can only be observed if the entire voltage scan is finished within an ultrashort time in which the redistribution of the ionic species in vicinity of the nanopore mouth is minimized.

Since the slope of the nearly linear $i-V$ curve of a silica nanopore is believed to reflect the ionic distribution at the initial voltage, it should change after the voltage perturbation is removed. It was thus interesting to study the $i-V$ response of silica nanopores under continuous voltage scans. Figure SI3 shows comparisons between the $i-V$ curves for the first and 5000th scan at $v = 1000$ V/s of an 8.7 nm silica nanopore in 10 mM KCl at pH 7.4 with three different initial voltages. First, no significant difference between the first and 5000th scans was observed when the scan was started at 0 V. This is because the distribution of ions is not shifted with a starting voltage of 0 V. When the scan was started at $+0.8$ V, however, the slope of the $i-V$ response increased to that for the 0 V starting voltage, indicating that the distribution of ions in the nanopore had returned to its "natural" state within 5000 scans. In the case of a starting voltage of -0.8 V, the slope of the $i-V$ response was observed to decrease with time, as expected. However, the rate of the slope change was significantly lower than in the $+0.8$ V case. This slower transition is not fully understood but could be due to a slower building-up process of the excess K^+ back to vicinity of the nanopore orifice when the negative voltage is removed, as compared with the the quick diffusion of K^+ out of the pore mouth from a higher concentration when a positive voltage is removed.

We studied cone-shaped silica nanopores of other diameters in the range $4-25$ nm (Figure SI4). No attempts were made in this study to investigate nanopores smaller than 4 nm or greater than 25 nm in diameter. A decrease in the rectification factor was observed in all of the nanopores in 10 mM KCl as the scan rate was increased. In addition, we studied the scan-rate-dependent current rectification of cone-shaped silica nanopores in other electrolyte solutions and found that the decrease in the rectification factor with increasing scan rate is not limited to KCl. For example, Figure 4a shows the $i-V$ response of a 4.2 nm silica nanopore in a 0.1 mM Tris buffer solution at pH 7.4 containing 10 mM $CaCl_2$ at scan rates from 10 to 1000 V/s. Figure 4b shows the rectification factor corresponding to the data in Figure 4a plotted as a function of the scan rate. The rectification factor was found to decrease from 2.5 at 10 V/s to 1.1 at 1000 V/s.
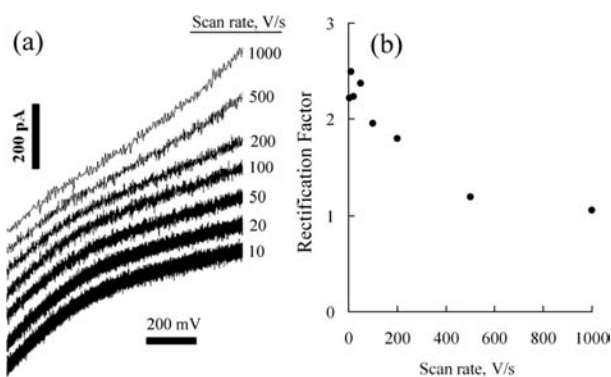
On the basis of the recent simulation results of White and Bund[3] and our experiments, we believe that a dynamic ionic redistribution could be responsible for the change in ionic conductivity and the observed current rectification behavior for cone-shaped silica nanopores. There have been numerous reports showing that the local concentration of an ionic species can be dramatically regulated in a cone-shaped glass nanopore even by a small bias voltage.[12−14] For example, Clarke et al.[12] showed that the concentration of a charged fluorescent dye in a glass nanopore can be increased by a factor of $\sim$3000 under a small bias voltage. Using fluorescent microscopy, they also showed that these charged molecules are in fact loosely localized at the pore mouth: a region of 8 μm from the pore mouth was measured under a 2 V bias voltage.[12]

The fact that a smaller rectification factor was observed at high v suggests that the redistribution of such concentrated ionic species in the nanopore can be sluggish relative to a quickly changing voltage perturbation. The redistribution of ionic species can be driven by diffusion, migration, and electroosmosis, the rates of all of which are proportional to the diffusivity of the ionic species, D. The length that K^+ ions ($D \approx 2 \times 10^{-9}$ m^2/s [15]) can diffuse in the time duration of a voltage scanning experiment at 100 V/s was estimated to be $\delta \approx 1.0$ μm, as determined using the Einstein relationship $\delta = (2Dt_{exp})^{1/2}$, where t_{exp} is the time duration of the voltammetric experiment.[16] In fact, a smaller diffusion coefficient of K^+ and therefore a smaller diffusion length δ can be anticipated in the vicinity of the nanopore mouth because of the high concentration. Without consideration of migration and electroosmosis, however, this simple calculation indicates that the distribution of the freely moving K^+ ions could be largely unchanged at the nanopore mouth, assuming that the excess K^+ occupies a similar region as reported by Clarke et al.[12] On the other hand, when a low scan rate (e.g., 0.1 V/s) is used, these ions would have sufficient time to redistribute inside the nanopore during the voltage scan. Under such conditions, the silica nanopore would exhibit regular current rectification behavior.

In summary, we have studied the $i-V$ response of cone-shaped silica nanopores in KCl solutions at high scan rates. Our results have shown that current rectification of a cone-shaped silica nanopore depends strongly on the rate of the voltage scan. At low scan rates, the nanopore exhibits strong rectification behavior. As the scan rate is increased, the $i-V$ response shows nearly ohmic behavior. In addition, we have shown that at very high scan rates, the $i-V$ response of a cone-shaped silica nanopore is largely determined by the initial voltage and has a slope close to that at the starting voltage. On the basis of these results, we believe that voltage-driven dynamic ion redistribution could be responsible for the current rectification behavior observed in cone-shaped silica nanopores. This redistribution can be slower than the rate of the voltage perturbation under ultrafast voltammetric conditions, which may explain the nearly ohmic behavior of silica nanopores.

Supporting Information Available: Full experimental details, an SEM image of a silica nanopore, and current−voltage responses of silica nanopores. This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 4. (a) Scan-rate-dependent $i-V$ responses of a 4.2 nm diameter silica nanopore in a 0.1 mM Tris buffer solution at pH 7.4 containing 10 mM $CaCl_2$. (b) Rectification factor in (a) plotted as a function of the scan rate. The pore diameter was calculated from the conductance in 1 M KCl assuming a half-cone angle of 5°.

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