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Conical-Nanotube Ion-Current Rectifiers: The Role of Surface Charge

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Ion channels are protein pores that span cell membranes and open and close in response to stimuli like changes in the transmembrane potential, binding of a ligand, or mechanical stress.[1] When open, ions pass through the pore, and when closed, ion-transport is precluded. Hence, these channels are nanodevices that have a current-rectification function. There is intense research effort aimed at understanding the molecular-level mechanism for this function.[2] Siwy et al. have shown that a polymeric membrane that contains a single conically shaped nanopore can also act as an ion-current rectifier.[3,4] They suggested that rectification might be an inherent property of a conical nanopore with fixed surface charge; however, because of the poorly defined nature of the chemistry and charge of the polymeric pores they used, they were not able to definitively elucidate the mechanism. Wei et al. have described an alternative ion-current rectifying system.[5]

We have used the template-synthesis method[6a] to deposit gold nanotubes[6b,c] into conical polymeric nanopores. The resulting conical Au nanotubes offer tremendous advantage for elucidating the current-rectification function because the charge and chemistry of the nanotube wall can be varied at will by judicious choice of electrolyte[6b] or by thiol chemisorption.[6c] This has allowed us to make conical Au nanotubes that rectify the ion current and, just as importantly, to definitively elucidate the mechanism of this function.

Poly(ethylene terephthalate) membranes (12 μm thick) that contained a single heavy-ion-induced damage track[7] were obtained from GSI (Darmstadt, Germany). The damage track was chemically etched to yield a single conical nanopore;[3,8] the large-diameter opening at one face of the membrane was ~600 nm, and the small-diameter opening at the opposite face was ~20 nm. Electroless Au plating[6c] was used to deposit a conical Au nanotube along the walls of this pore. This decreased the small-diameter opening to ~10 nm but did not appreciably change the large-diameter opening. Details of the etching, plating, characterization, and thiol chemisorption procedures are presented in Supporting Information.

The single conical Au nanotube membrane was mounted between the two halves of a conductivity cell,[3,8] and a Ag/AgCl electrode was inserted into each half-cell solution. Current–voltage (I–V) curves associated with ion transport through the nanotube were obtained using an Axopatch 200B (Axon Instruments). The working Ag/AgCl electrode was in the half-cell solution facing the large-diameter opening, and the potential of this electrode was controlled relative to the counter Ag/AgCl electrode in the opposite solution. The potential was stepped in 100 mV steps through the desired potential range, and the resulting transmembrane ion current was measured.

Figure 1 shows I–V curves for conical Au nanotubes using either 0.1 M KCl or 0.1 M KF as the electrolyte solution in both half-cells. In KF the nanotube shows an ordinary linear, ohmic, I–V curve.[9] In KCl the nanotube rectifies the ion current; i.e., at any absolute value of transmembrane potential, the current is higher at negative potentials ("on" state) than at positive potentials ("off" state).
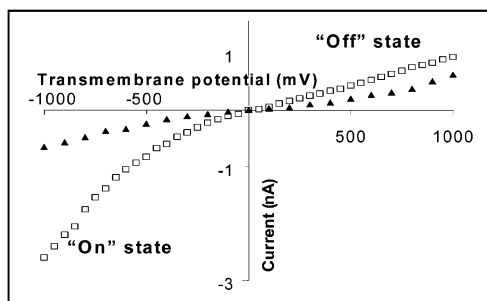

Figure 1. I–V curves in 0.1 M KCl (□) and 0.1 M KF (▲).

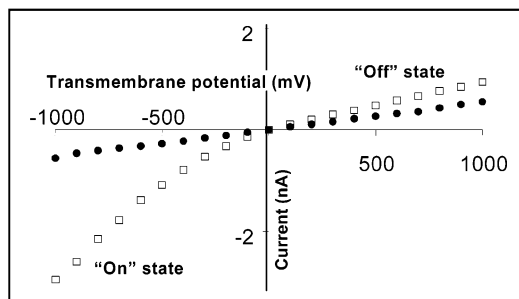**Figure 2.** I–V curves in 0.1 M KF for gold nanotubes modified with 2-mercaptopropionic acid; pH = 6.6 (□) and pH = 3.5 (●).

While F⁻ does not adsorb to Au surfaces, Cl⁻ does, and it has a charge of −1 in the adsorbed state.[6b] Hence, Figure 1 suggests that rectification requires surface charge.[4] To explore this issue further, analogous experiments were conducted in 0.1 M KF using a conical Au nanotube containing the chemisorbed thiol mercaptopropionic acid (Figure 2). At pH = 6.6, the −COOH group is deprotonated, yielding negative surface charge, and rectification is observed. That this is due to carboxylate is confirmed by the fact that the non-thiol-treated nanotubes do not rectify in KF (Figure 1). Furthermore, at pH = 3.5, the surface charge is removed by protonation of the carboxylate, and rectification is not observed (Figure 2).

Figures 1 and 2 show that the Au nanotube can be regarded as a blank slate into which the current-rectification function can be added or removed at will. These data also show that surface charge on the nanotube wall is essential for observing this function.[3-5] A clue to the mechanism is found in the relative magnitudes of the currents for a nanotube that rectifies vs the corresponding nanotube that does not. The "on" state current for the rectifying nanotube is much greater than the corresponding current for the nonrectifying tube. Furthermore, the rectifying nanotubes show higher currents even at positive transmembrane potentials when they are in their "off" state.

If the radius of a nanotube containing fixed anionic surface charge is comparable to the thickness of the electrical double layer within the tube, engendered by this charge, then the tube will preferentially incorporate cations (K⁺) and reject anions.[6b] Furthermore, the K⁺
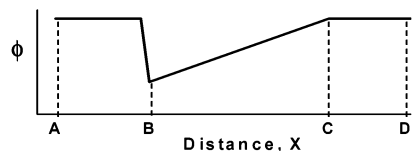
Figure 3. Schematic of the electrostatic potential for a cation in and near a conical Au nanotube with a fixed negative surface charge.

concentration within the tube will be higher than the 0.1 M concentration in the contacting solutions.[5] We have shown that this is true for the nanotubes with adsorbed Cl^- by using a potentiometric method to measure the K^+ transference number, t_+.[6b] A t_+ value of 0.8 was obtained, indicating that the tubes do, indeed, reject Cl^- and preferentially incorporate K^+. This *enrichment in charge-carrier (K^+) concentration* explains why the rectifying (charged) nanotubes support higher currents than their nonrectifying counterparts.

However, in these conical nanotubes, only a region near the small opening has a radius that is comparable to the double-layer thickness. Hence, in the absence of a transmembrane current, the electrostatic potential (ϕ) experienced by a cation as it traverses the nanotube has a form like that shown in Figure 3.[4] The portion from A to B represents the solution in contact with the small-diameter opening of the nanotube, and since there is no current, ϕ is constant. The line from B to C represents the part of the conical nanotube where the radius is comparable to the double-layer thickness. In this region, the potential of the cation is lowered due to electrostatic interactions with the fixed anionic surface charge. Since the nanotube diameter increases in the X direction, this electrostatic stabilization falls off with increasing X, accounting for the upward slope from B to C. The portion from C to D represents the part of the nanotube where the radius is much greater than the double-layer thickness.

When a potential of +E volts is applied across the membrane, the voltage drop caused by the resulting positive current effectively turns Figure 3 (e.g., $^1/_4$ turn) in the counterclockwise direction. As shown in Supporting Information, this creates an electrostatic trap for the cation at point B, and it is this trap that causes rectification ("off" state) at positive potentials. When a potential of −E volts is applied, the resulting negative current causes Figure 3 to be turned (e.g., 1/4 turn) clockwise, and there is no electrostatic trap. As a result, the "on" state is observed at negative potentials.

This simple electrostatic-trap model explains all of the experimental data we have obtained from a variety of different Au nanotube systems. First, we have found that cylindrical nanotubes (with the same electrolyte on both sides of the membrane) never rectify;[9] this is because there is no asymmetry in the electrostatic potential in a cylindrical nanotube. Second, conical nanotubes where the radius of the small-opening is greater than ~15 nm also do not rectify. This is because this radius is much larger than the double-layer thickness for the electrolyte concentration used here.[6b] Finally, adding positive surface charge to our small-diameter conical nanotubes should yield rectifiers with polarity opposite that of the anionic nanotubes. Figure 4 shows that this is also true.

Siwy et al. suggested this model as a possible explanation for rectification in their conical polymeric nanopores.[3,4] However, in
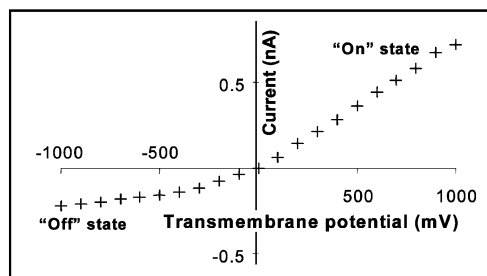

Figure 4. $I-V$ curve in 0.1 M KF (pH = 6.6) for gold nanotubes modified with the mercaptoethylammonium cation.

this case, the fixed charge is present as carboxylate groups on the dangling ends of the polymer chains. For this reason, they could not discount a second possible model that involved sweeping these charged chain ends into and out of the small-diameter opening of the nanopore. Our results with adsorbed Cl^- and short-chain thiols clearly show that this mechanism is not operative in the Au nanotube case.

The voltage-gated potassium channel also has a conical shape, and quantum or molecular mechanics calculations show that, like Figure 3, there is a deep electrostatic minimum for cations at one end of the channel.[2c] Furthermore, Figure 3 is an example of an electrostatic "ratchet", and the importance of this potential profile to ion pumping in ion channels has been recognized.[10] Nevertheless, it is clear that rectification in biological channels involves physical movement of charged segments of the protein in response to a change in the transmembrane potential.[2a] Preparing conical nanotubes that mimic this function is a goal of our future research effort.

Supporting Information Available: Preparation of the single conical gold tubes and the ratchet model (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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