Numerical Modeling of the Bistability of Electrolyte Transport in Conical Nanopores

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Abstract

Nanochannels are solid-state or biological channels with nanometer-scale dimensions. A characteristic feature of nanochannels is that surface properties (e.g., electrical charge) play a more significant role in the transport of fluid and electrolyte. Interesting transport phenomena in nanochannels, which do not occur at large length scales, have been observed during the past decade. A better understanding of these behaviors is important due to the importance of nanochannels in biological system, as well as in developing new chemical sensing technologies.

The nanochannel that our laboratory has studied is a conical nanopore embedded in a glass membrane with a half cone angle of ~10°, as illustrated in Figure 1. When the nanopore is immersed in an electrolyte solution and a voltage (~1 V) is applied, a very large electric field (~10^5 V/m) develops at the small orifice. This voltage drop is due to its higher electrical resistance at the orifice. This electric field generates a strong electroosmotic flow (EOF) at the negatively-charged glass nanopore wall (Figure 2, white arrow). When a small pressure (1 to 50 mmHg) is applied across the nanopore, the EOF and pressure-driven flows have comparable rates and oppose one another. The two oppositely directed flows determine the flow profile at the nanopore orifice as well as electrolyte distribution. We have discovered that when the internal and external solutions contain different concentrations of KCl, the current-voltage (i-V) curves display a bistability between two conductivity states. As shown in Figure 3a, a sudden drop in the nanopore current occurs within an ~ 0.5 mV potential window. A high-conductivity state exists at voltages positive of the bistability voltage, and a low-conductivity state exists at potentials negative of the bistability voltage.

We used COMSOL Multiphysics® to model the bistability in the i-V response by simulating the ion transport and fluid flow in the nanopore under the influence of pressure and electric forces. Figure 3b show the simulated i-V plot, which semi-quantitatively reproduces the experimental observations. The small discrepancy between the simulated and experimental i-V curve is likely due to uncertainty in the nanopore geometry. Our simulations of the voltage-dependent steady-state fluid velocity profiles and ion concentrations demonstrate that the conductivity bistability is due to a positive feedback loop between EOF and the local concentration at the nanopore orifice. Also, our model indicates a very sensitive dependence of the bistability voltage on the surface charge density, suggesting application of the nanopore bistability in physical or chemical sensing. For instance, addition of Ca^{2+} to the electrolyte solution leads to a ~1 V negative shift in the bistability voltage, due to strong binding of Ca^{2+} to the negatively charged glass walls.

In summary, the COMSOL simulations capture an unusual bistability associated with complex ion transport and fluid flow within a nanochannel. We are currently employing COMSOL to model the dynamics of the positive feedback loop as well as developing biosensors based on the nanopore conductivity switching.

Figures used in the abstract

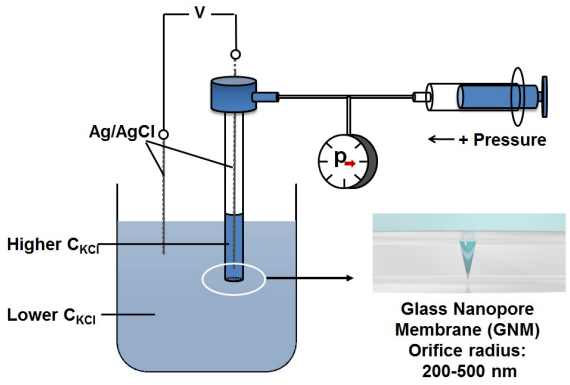

Figure 1: Schematic illustration of experimental setup to study the conductivity bistability in a conical nanopore embedded within a glass membrane.

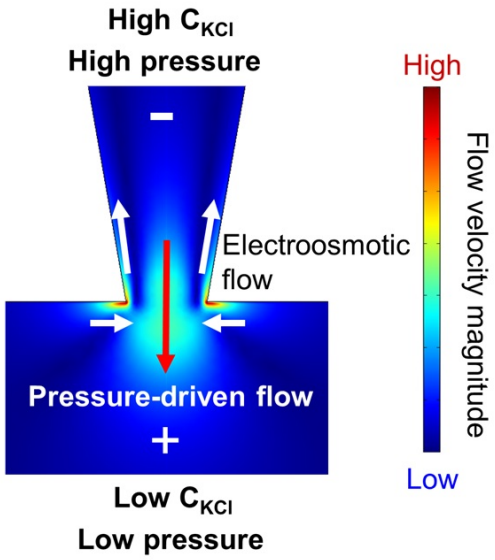

Figure 2: Simulated velocity profile at a nanopore, involving electroosmotic flow (EOF, white arrow) along the nanopore surface opposing pressure-driven flow in the center of the nanopore (red arrow).

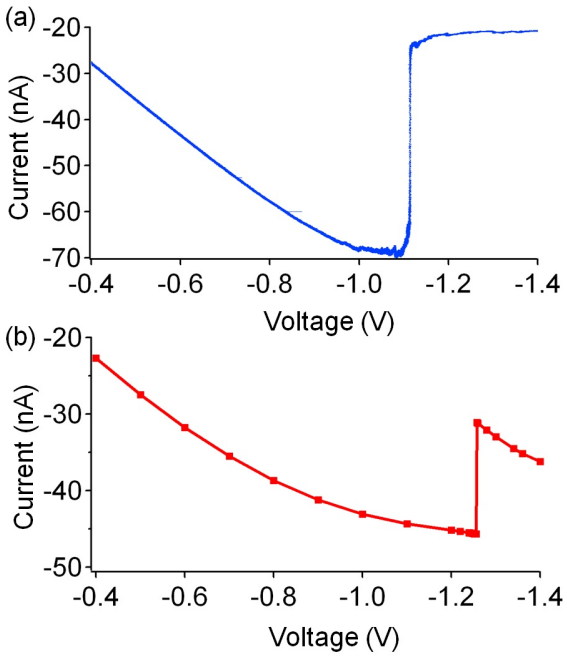

Figure 3: (a) Experimental i-V curve showing a sudden drop in current while increasing the voltage across a nanopore and holding the pressure constant. The bistability occurs within a very narrow voltage window (~1 mV). Scan rate: 20 mV/s, pressure: 10 mmHg. (b) Simulated i-V response using same conditions as the experiment in (a).