# Numerical Modeling of the Bistability of Electrolyte Transport in Conical Nanopores

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**Introduction**:

A characteristic feature of nanochannels is that surface properties (e.g., electrical charge) play a more significant role in the transport of liquids and electrolyte ions. Interesting transport phenomena in nanochannels, which do not occur at large length scales, have been observed during the past decade.

We studied conical nanopores in a glass membrane that have a small orifice radius between 100 and 500 nm. The experimental setup is shown in Figure 1. When a small pressure (1 to 50 mmHg) and a negative voltage (internal vs. external) is applied across the nanopore, we discovered that the current-voltage (i-V) curves displays a bistability between two conductivity states, as shown in Figure 2. This bistability corresponds to a negative differential resistance and is important in biosensor development.
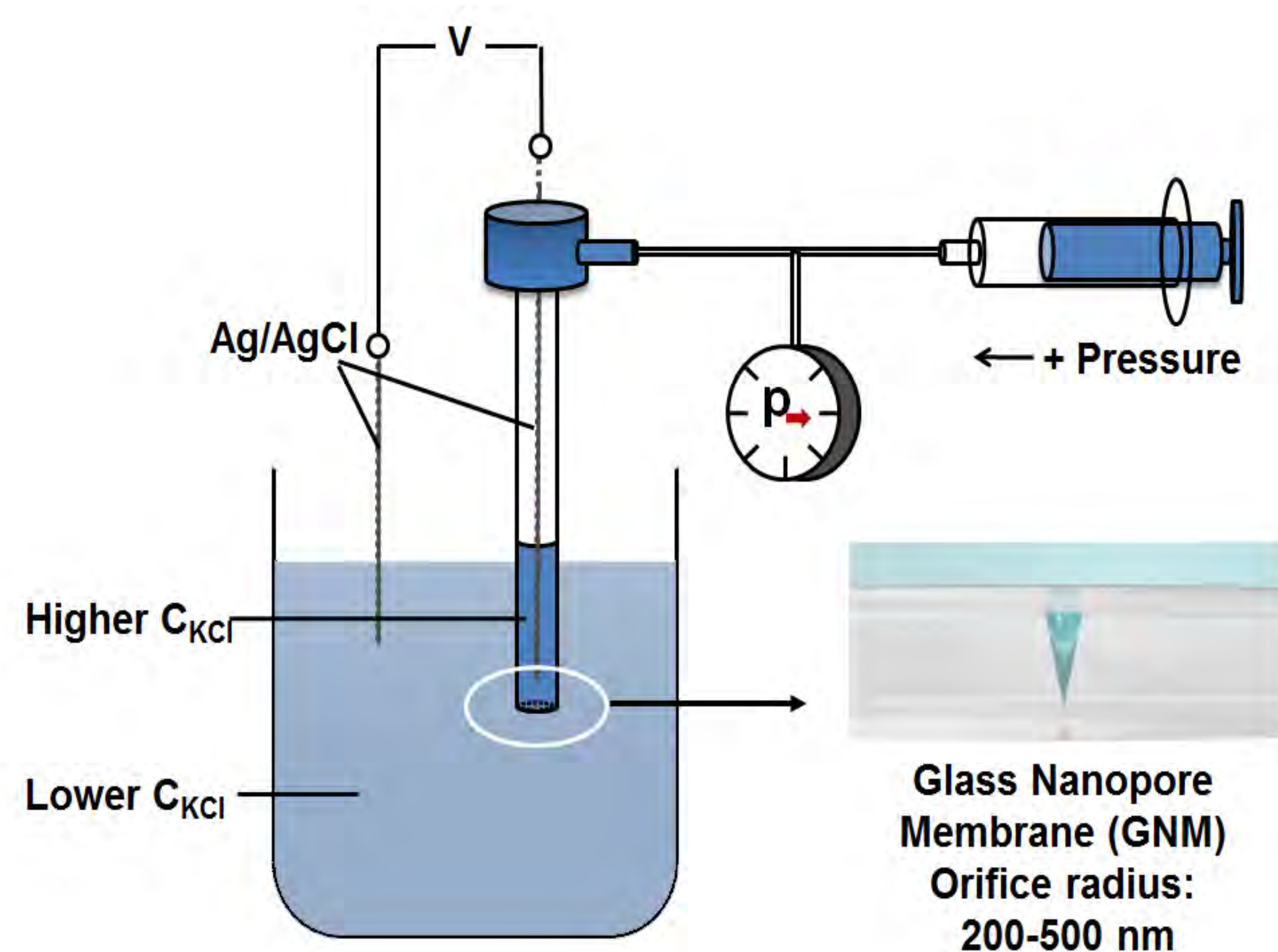


**Figure 1**. Schematic of experimental setup to study the conductivity bistability in a conical nanopore within a glass membrane.
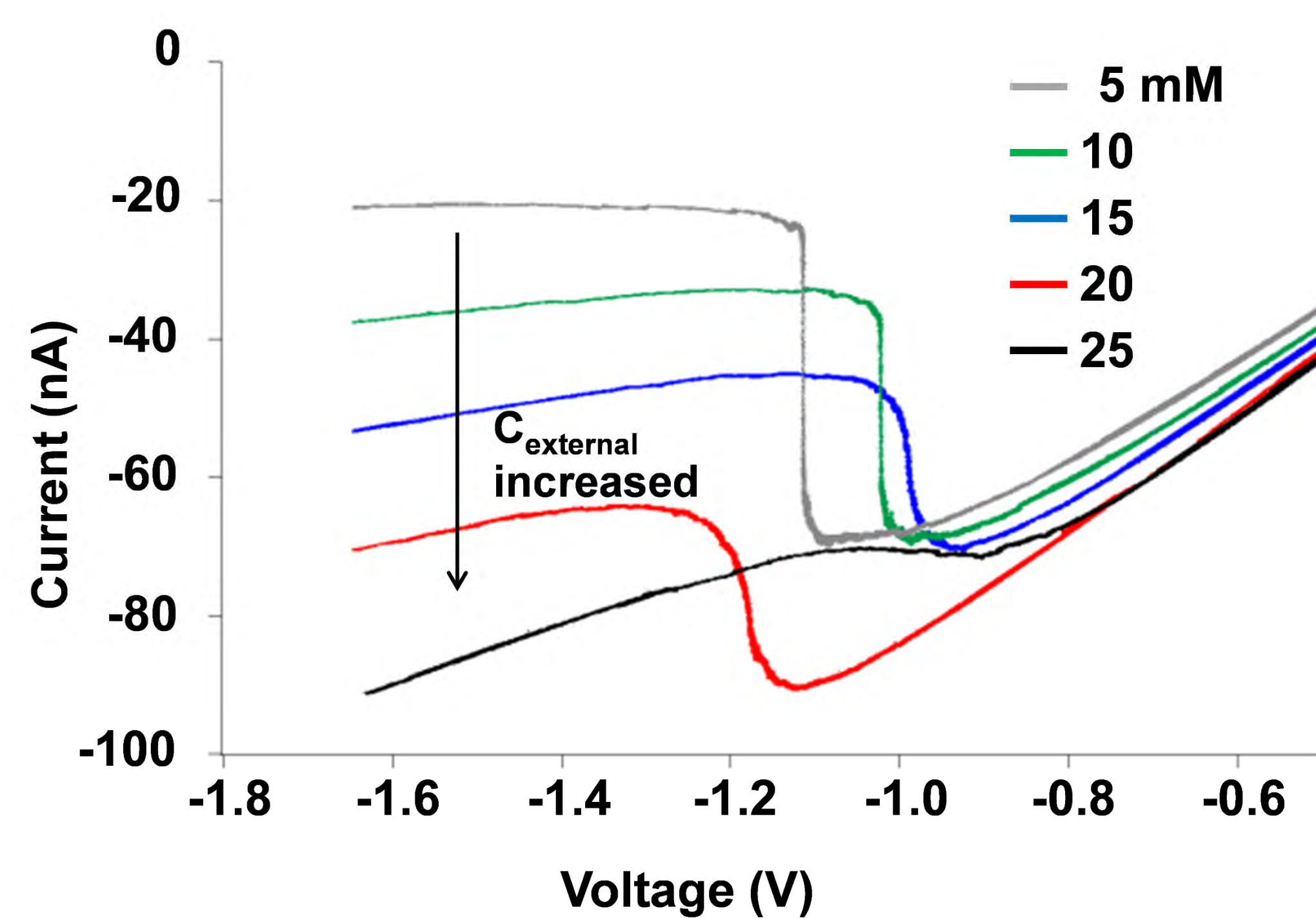


**Figure 2.** A series of current-voltage curves measured with a 260 nm radius nanopore; external KCl solution concentration of 5-25 mM and internal KCl solution concentration of 50 mM. Pressure = 10 mmHg (internal vs. external).

**Computational Methods**: Steady-state finite element simulations using COMSOL Multiphysics were performed to provide a quantitative model of the experimental results.

1) *Navier-Stokes equation* describing pressure and electric force driven flows.

$$\mathbf{u}\nabla\mathbf{u} = \frac{1}{\rho}(-\nabla p + \eta\nabla^2\mathbf{u} - F(\sum_i z_i c_i)\nabla\Phi)$$

2) *Nernst-Planck equation* describing the diffusion, migration and convection of ions in the nanopore.

$$\mathbf{J}_i = -D_i\nabla c_i - \frac{Fz_i}{RT}D_i c_i\nabla\Phi + c_i\mathbf{u}$$

3) *Poisson's equation* relating the nanopore surface charge to the distribution of ions within the nanopore.

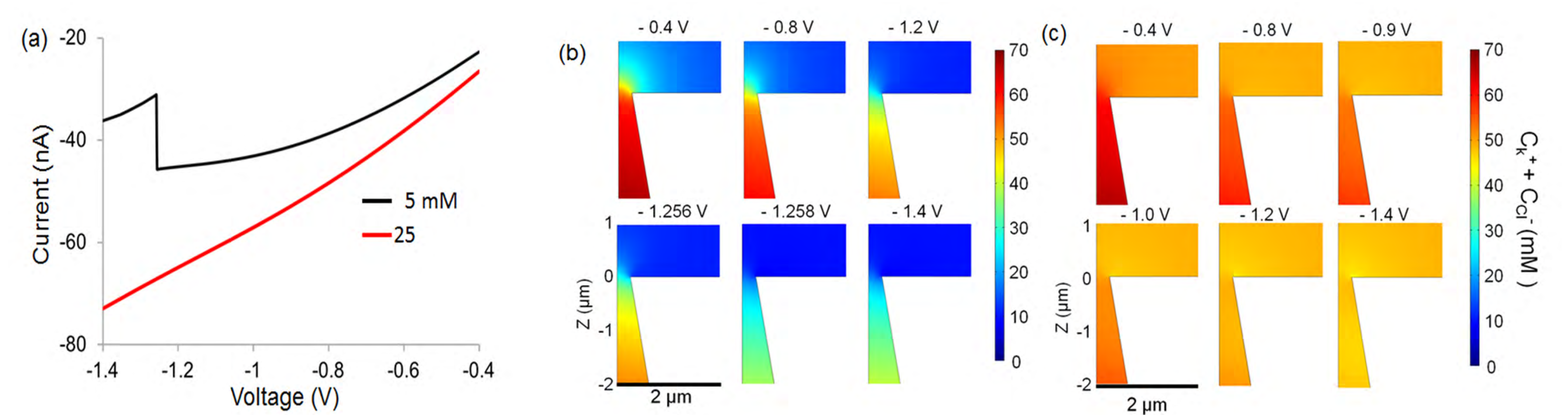$$\nabla^2\Phi = -\frac{F}{\varepsilon}\sum_i z_i c_i$$

**Results:**



**Figure 3.**(a) Simulated i-V curves with external KCl concentration of 5 or 25 mM and internal concentration of 50 mM, corresponding to the grey and black lines in Figure 2, respectively. Surface charge density on the nanopore: -12.5 mC/m². (b) and (c) are the total ion concentration profiles for external KCl concentrations of 5 and 25 mM, respectively.
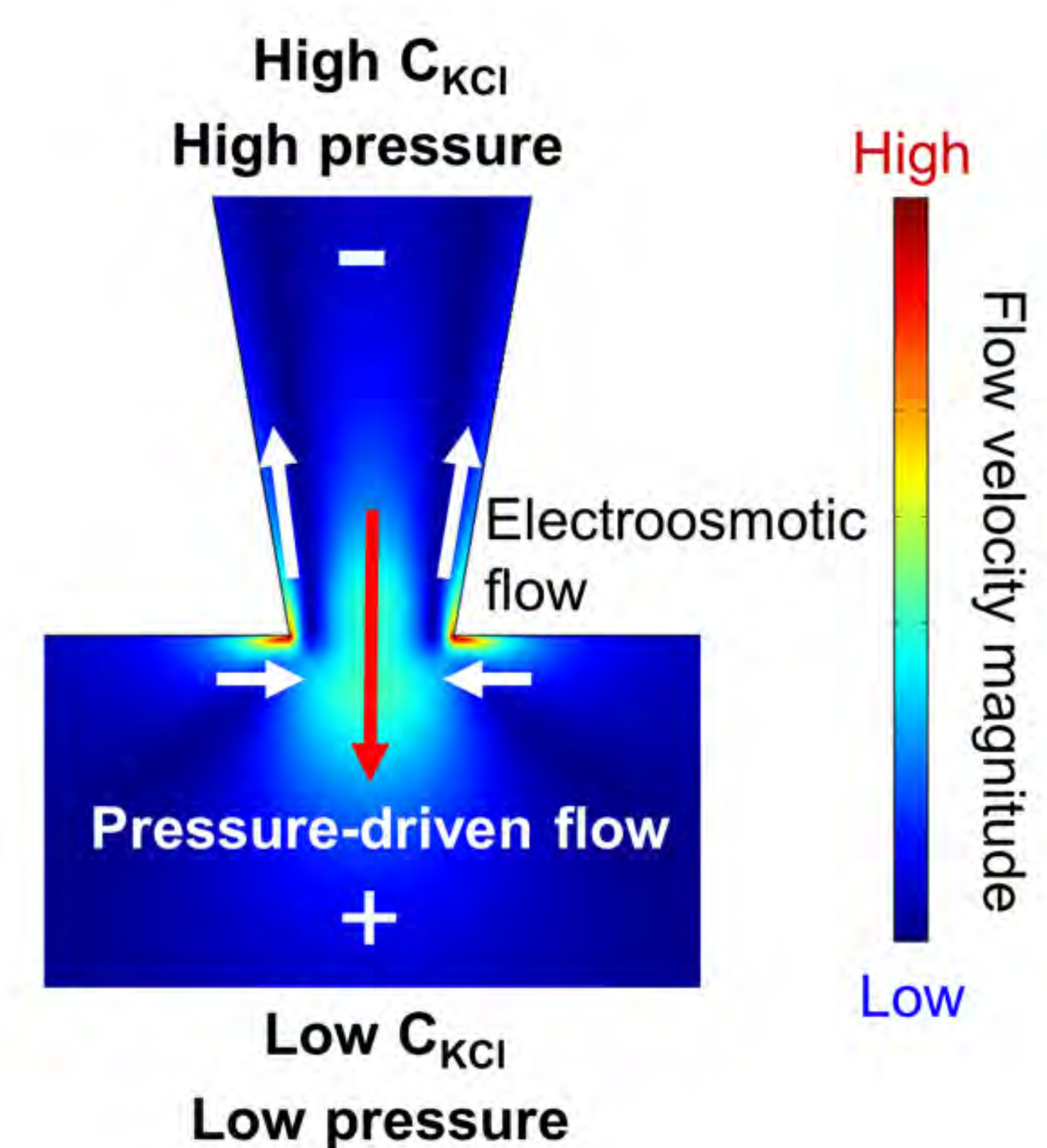


**Figure 4**. Simulated velocity profile at a nanopore, involving electroosmotic flow (white arrow) and pressure-driven flow (red arrow).
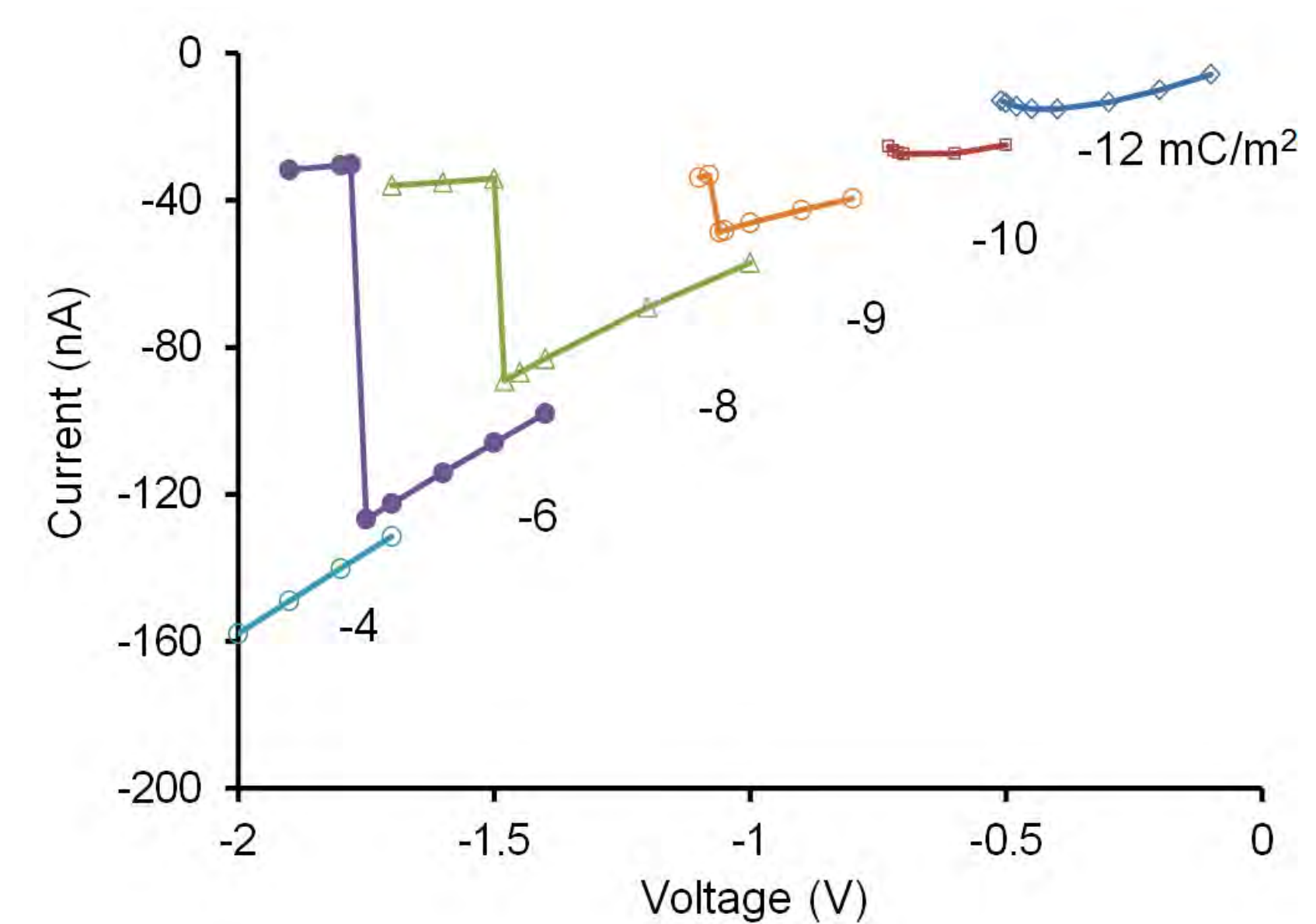


**Figure 5.** Simulated i-V curves in a 260-nm-radius nanopore with 5 mmHg pressure applied and various nanopore surface change density.

**Conclusions**

1) The model semi-quantitatively captures the experimental observations and demonstrates that the sudden drop of current is caused by a ion distribution bistability, as shown in Figure 3.

2) The conductivity bistability is caused by the competition between electroosmotic flow (white arrow) and pressure-driven flow (red arrow), as shown in Figure 4. The two oppositely directed flows determine the flow profile at the nanopore orifice as well as electrolyte distribution.

3) Figure 5 shows a sensitive dependence of the i-V curve on surface charge density, indicating potential applications as sensors.

**References**:
1. White, H. S. et al. Ion current rectification at nanopores in glass membranes, Langmuir, 24, 2212-2218.(2008)
2. Luo, L. et al. Tunable Negative Differential Electrolyte Resistance in a Conical Nanopore in Glass, ACS Nano, 6, 6507-6514.(2012)