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Overlimiting current near a nanochannel a new insight using molecular dynamics simulations

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Abstract

In this paper, we report for the first time ion concentration polarization (ICP) near a nanochannel using all-atom molecular dynamics (MD) simulations. Here, the simulated system consists of a silicon nitride nanochannel integrated with two reservoirs. The reservoirs are filled with 0.1 M potassium chloride (KCl) solution. A total of ~1.1 million atoms are simulated with a total simulation time of ~0.8 μs over ~27000 CPU hours using 128 core processors (Intel(R) E5-2670 2.6 GHz Processor). The origin of overlimiting current is found to be due to an increase in chloride (Cl^-) ion concentration inside the nanochannel leading to an increase in ionic conductivity. Such effects are seen due to charge redistribution and focusing of the electric field near the nanochannel and source reservoir. Also, from the MD simulations, we observe that the earlier theoretical and experimental postulations of strong convective vortices resulting in overlimiting current are not the true origin for overlimiting current. Our study may open up new theories for the mechanism of overlimiting current near the nanochannel interconnect devices.

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Introduction

Nanochannels are used for many applications such as seawater desalination[1], biomolecule preconcentration, nanofluidic diode, and DNA sequencing [1]. Nanochannels are typically integrated with two reservoirs and a potential difference is applied across the reservoirs. The ion selectivity of the nanochannel is controlled by the surface charge density of the nanochannel and thickness of the electrical double layer (EDL). When the solid wall of the nanochannel comes into contact with electrolyte solution, the surface charge density of the nanochannel induces an electric potential. Ions are redistributed according to the potential and form an electrical double layer (EDL) [1]. The application of potential difference across the nanochannel creates an imbalance between cation and anion flux leading to the formation of the depletion and enrichment of the electrolyte solution across the interface of the nanochannel resulting ion concentration polarization (ICP) [1]. The ion concentration polarization (ICP) effect leads to nonlinear I-V characteristics resulting in three regions, namely, Ohmic region, limiting resistance region (LRR) and overlimiting region (OLR). Owing to the advancements in micro/nanofabrication technology, many experimental investigations have been conducted to understand the finite resistance in the limiting resistance region and the transition from the limiting resistance region to the overlimiting resistance region [1]. It is observed that the formation of strong convective vortices in the depletion side of the nanochannel decreases the length of the depletion diffusion boundary layer (DBL) and decreases the resistance that results in the overlimiting resistance region. To find out the true mechanism, here, we report molecular dynamics (MD) simulations [2] to understand overlimiting current near a nanochannel for the first time.

Simulation Details

A typical simulation system includes a silicon nitride nanochannel integrated with two reservoirs filled with 0.1M potassium chloride (KCl) solution. The final assembled simulation system and the direction of the applied electric field is shown in Figure 1. Based on the direction of the electric field, we classify the left and right side reservoirs as the source and sink reservoirs, respectively.

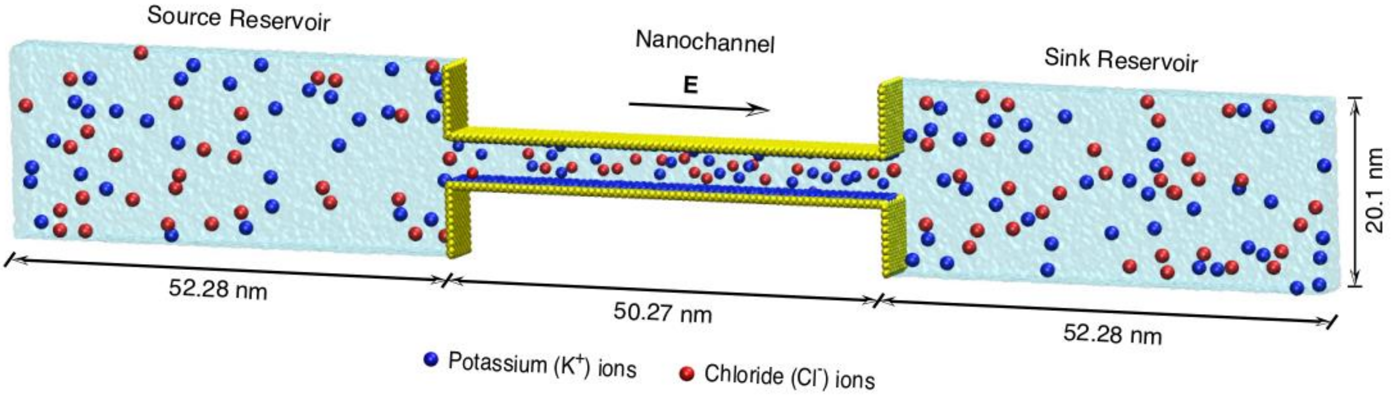

Fig. 1. MD snapshot of silicon nitride nanochannel integrated with two reservoirs filled with 0.1M potassium chloride (KCl) solution.

A voltage range of 5 V - 200 V is applied across the ends of the reservoirs. The ionic current is measured inside the nanochannel [2],

Numerical Results

In the Ohmic region, we observe that the electric field is high inside the nanochannel compared to both the reservoirs because of high electrostatic interactions between the adsorbed cations and negatively charged wall atoms along with applied voltage and electrolyte KCl solution. In the limiting resistance region, the current deviates from the Ohm's law, but the current does not saturate as predicted by the classical diffusion-limited current transport theory but increases slowly with applied voltage [1]. In this region, the electrostatic interactions with adsorbed ions and freely moving electrolyte KCl solution creates a region of extended charge region between the nanochannel and source reservoir (see Figure 2).

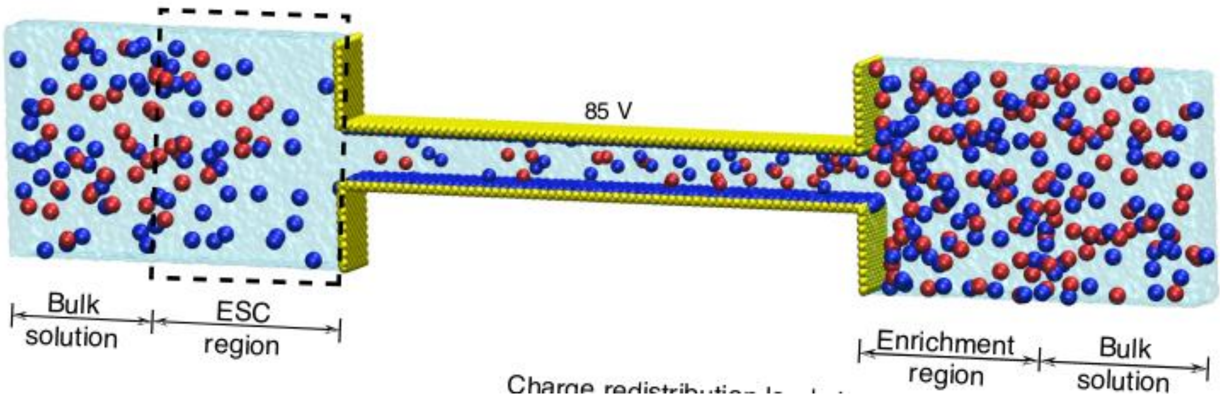

Fig. 2. MD snapshot of extended charge region between the nanochannel and source reservoir, in the limiting resistance region.

In the overlimiting resistance region, the current again increases linearly like the Ohmic region. We observe the propagation of the ESC region towards the source reservoir. Also, we observe the propagation of the enrichment region inside the sink reservoir. The propagation of the ESC region towards the source reservoir increases the strength of the normal component of the focused electric field. Furthermore, this focused electric field allows the ESC region to propagate into the nanochannel. The charge redistribution mechanism due to the ESC propagation towards the source reservoir and into the nanochannel changes the chloride (Cl^-) ion concentration inside the nanochannel resulting in an increase in ionic conductivity and causes the overlimiting current (see Figure 3.).

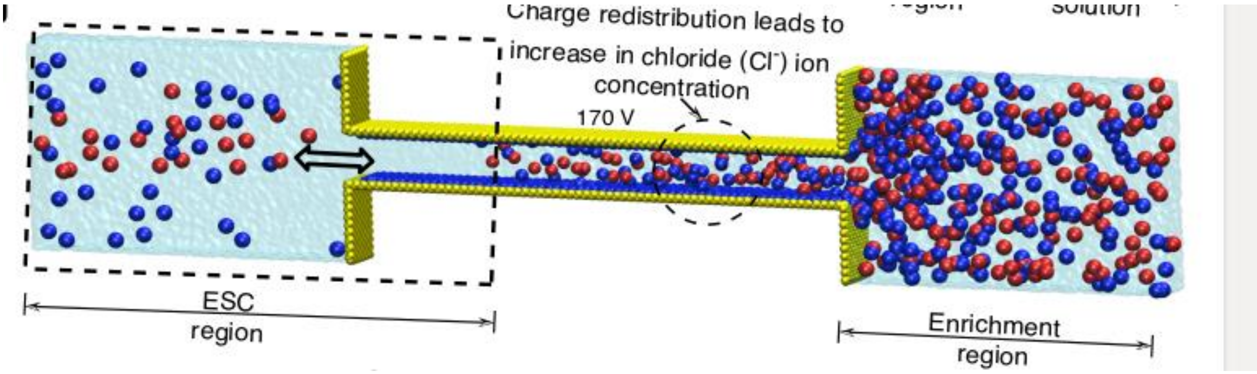

Fig. 3. MD snapshot of charge redistribution resulting in Overlimiting region.

Furthermore, to test if convective vortices are the reason for the overlimiting current, we performed a hypothetical MD simulation with KCl molecules (powder) and not KCl solution (KCl + water). For the hypothetical MD simulation, the dielectric constant was set to be 79 [2]. We still observe the formation of the ESC region and charge redistribution with overlimiting region and overlimting current. We infer from these observations that the charge redistribution is the true mechanism for the overlimiting region and overlimiting current and not the strong convective vortices as postulated by earlier experiments and theories [1]. To demonstrate if the ion selectivity of the nanochannel plays a role on ion concentration polarization, we increased the bulk concentration from 0.1 M to 1 M. With an increase in bulk concentration, we observe only the Ohmic region because the nanochannel is no longer ion selective at 1M KCl concentration.

Conclusions

In this paper, we provide for the first time the true origin mechanism for overlimiting region and overlimting current near the nanochannel using MD simulations.

References

1. D. Manikandan and Vishal Nandigana, Ion Concentration Polarization (ICP): From Ion Exchange Membranes to Micro/Nanofluidic Interconnect Devices - A Complete Review, International Journal of Science and Research (IJSR), Volume 10, Issue 6, June 2021.

2. https://www.ks.uiuc.edu/Research/namd/ NAMD, scalable molecular dynamics package.