Concentration Polarization of High Concentration Solution in Sub-nm Nanopore

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Abstract. The behavior of ion transport through the sub-nm nanopores on the film is different from the behavior of bulk behavior. Many intriguing phenomena in ionic transport are the key to the design and fabrication of solid-state nanofluidic devices. However, ion transport through the sub-nm nanopores is not yet clearly understood. We investigate ionic transport of sub-nm nanopore from the perspective of conductance by the method of MD. The results show that the ion concentration polarization phenomenon is heavily dependent on the external electric field and the size constraints of nanopores. At the same time, ion concentration polarization also has a profound effect on ion conductance. These conclusions indicate that ion concentration polarization has an important influence on ion transport, and help a new understanding of the design of nanofluidic devices.

1 INTRODUCTION

Due to many intriguing phenomena in ionic transport, for example, ion selectivity^{1,2}, ionic field-effect³, and ionic current rectification⁴, design and fabrication of solid-state nanofluidic devices have elicited increasing attention to both the scientific and engineering communities⁵⁻⁷. Electric control of ionic transport is of primary importance for the design of novel nanofluidic devices, such as sensing devices⁸, water desalination⁹, and energy conversion¹⁰. Many studies have shown that ionic transport in nanoconfinement is mainly controlled by the following factors: (1) geometry, (2) surface charge, (3) chemical composition, (4) wettability, (5) environmental pH, (6) electrolyte concentration gradient, (7) ion mobility, and (8) electric field strength¹¹. Factors 1-4 are determined by design and fabrication of nanopore, while factors 5-8 can be tuned in the electrolyte solutions. How to exploit these factors in subtle ways is key to design nanofluidic devices.

Ion transport through graphene nanopore is a common and important theme in various applications. Numerous theoretical and experimental research have been developed in recent years¹²⁻¹⁴. Molecular dynamics (MD) simulation is an effective tool to allow the physical mechanisms underlying this behavior to be elucidated. Many researchers have studied ion transport through nanopores, using molecular dynamics. Bordin, J.R., et al.¹⁵ studied ion transport in modified carbon nanotubes. Chen, Y.F., et al.³ reported electro osmotic flow in nanotubes with high surface charge densities. Suk, M.E., et al. and Hu, G., et al. focused ion mobility and ion concentration polarization (ICP) in graphene nanopore^{16,17}. As a

consequence, molecular dynamics is also useful tool to observe atom level behavior of ions.

Despite being widely used, many properties of nanopore have not been well understood, especially in a nanopore which the pore diameter is comparable to the atom diameter. Some properties which may deviate from the bulk properties and continuum theory cannot be used to account for experimental data¹⁸. A typical experimental set-up is that of a small pore located in a thin graphene barrier which separates two chambers (henceforth called cis. and trans.). Electrolyte solution is added into each chambers and an external voltage drop which is formed by inserting two electrodes into aqueous cis. and trans. chambers drive molecular and ions through the pore. The fundamental principles of several applications, especially sensing or analyzing biomolecules, is that measure the ionic current. Thus, an important characterization of nanopore is conductance. Many studies have shown a power-law relationship between ion concentration and ion conductance. Therefore, probing the influence of ion concentration polarization on ion conductance is beneficial for a clear understanding of ion transport in sub-nanopores.

2 Method

In this study, ion concentration polarization layer is investigated with molecular dynamic (MD) simulation. The system selects a cube box as the research unit, the box size is: $L_x=5.28\text{ nm}$, $L_y=5.39\text{ nm}$, $L_z=10.60\text{ nm}$. The conditions is electric field strength $E=0.0.3/0.5\text{ V}/1\text{ V nm}^{-1}$, the NaCl concentration 0.1/0.5/1/2/3/4M, and nanopore diameter $D=0.5/1/2/3/4\text{ nm}$, where $z=5.3\text{ nm}$ corresponds

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to the graphene sheet. The bond length between carbon atoms is 0.142 nm, and the box is filled with TIP3P model water molecules. The system model is completed by the cooperation of the software GROMACS 5.02 and VMD(Figure 1).

Figure 1. Water and ions passing through graphene nanopore. (a).Schematic diagram of water and ions passing through graphene nanopore model. (b).graphene nanopore; (c). Water molecule model. (d). Ions and graphene.

All parameter settings refer to earlier reports^{17,19}. After the experiment is over, a comparison with some of the reported results verifies the feasibility of the experiment. The system temperature is stable at 300 K. The pressure is at 1 atmosphere. The temperature coupling method is the V-rescale method, and the pressure coupling method is the Parrinello-Rahma method. The simulation uses the OPLS all-atom force field, and the van der Waals interaction between ions is calculated by the Lennard-Jones (LJ) model. The cutoff radius is 1.0nm, while the Coulomb electrostatic interaction is calculated by the PME (particle-mesh Ewald) method. The cutoff distance is 1.0 nm. In order to drive the ions to move directionally in the system, a uniform electric field is applied in the Z direction. The atoms along the four edges of graphene are fixed. The time interval of each step of the system simulation is 2 fs, and the total number of steps is 5 million steps. The data storage frequency is 0.2 ps, and the total running time of the system is 10 ns.

3 Results & Discussion

Figure 2. Axial average distribution of ion number density. (a). Axial average distribution of Na⁺ number density. (b). Axial average distribution of Cl⁻ number density.

3.1 The influence of electric field intensity on concentration polarization

Figures 2a and b illustrate the functional relationship between the ion number density and the axial distance of the nanopore. In 1M NaCl solution, we applied a low-to-high electric field(0.3 Vnm⁻¹, 1 Vnm⁻¹, 3Vnm⁻¹) to the nanopore system, and then investigated how to control ion concentration polarization by Electric field strength. It can be clearly observed that ions form a dynamic region of enrichment and depletion at both ends of the nanopore. For Na⁺ and Cl⁻, the front and back ends in the electric field direction of the nanopore respectively form concentration extreme regions. And this phenomenon is concentration polarization.

Due to the distance between ions and graphene, there is a certain distance between ions and the center of carbon atoms in graphene. The combination of steric interactions (range, 0.1–2 nm), van der Waals forces (range, 0.1–50 nm) and electrostatic forces (range, 1–100 nm)^{3,20} result in the appearance of a concentration peak. When the electric field intensity is 0.3 Vnm⁻¹, 1 Vnm⁻¹, 3Vnm⁻¹, the distance of the peak Na⁺ concentration from the graphene position is 0.70nm, 0.64nm, 0.49nm, respectively. The interesting phenomenon is that the position of the peak chloride ion concentration from the graphene position is always about 0.21nm, when the electric field intensity changes. At the same time, the peak value is different. When the electric field intensity is 3v, the extreme value of Cl⁻ concentration is about twice that of Na⁺. There are two main reasons for this phenomenon. One is that the potential drop at both ends of the hole increases. In order to keep the internal electric field in the box in balance with the external electric field, the polarization of the ions increases. On the other hand, the potential drop at both ends of the pore polarizes the water molecules, and the density on both sides of the film is extremely high, making it more difficult for ions to compete for entrance.

Figure 3. The ratio of the pore concentration to the body concentration as a function of electric field. The stronger the electric field, the more significant the ion concentration polarization phenomenon. And the concentration polarization phenomenon of chloride ion has a higher rate of change than sodium ion.

To further investigate the relationship between concentration polarization and electric field, we compared the peak concentration with the bulk concentration value (Figures 3). In the low voltage area, the concentration polarization phenomenon is not obvious. When the voltage is greater than 0.6 V/nm, the concentration polarization peak increases rapidly. At 3 V/nm, the number density of chloride ion and sodium ion polarization area is 20.11 and 11.79 times the average number density of the system, respectively, and the polarization rate of chloride ion concentration is higher than that of sodium ion. With the increase of voltage, the reason for the rapid increase in the number density of the concentration polarization zone has been studied to show that vortex currents are formed on both sides of the graphene film, which strengthens the ion current¹⁷.

3.2. The effect of size constraints on concentration polarization

Ion dynamics in a charged nanopore with dimensions comparable to the Debye length (sub-nm nanopore) deviate from the bulk values^{21,22}. Similar phenomena, referred to as charge overspill²³, and electroneutrality breakdown²⁴, have been extensively reported. In Figure 4, we can clearly observe that the smaller the diameter of the nanopore, the more obvious the ion concentration polarization phenomenon. When the diameter of the nanopore is greater than or equal to 3nm, the peak concentration difference between sodium ions and chloride ions in ion concentration polarization phenomenon disappears. However, the concentration polarization phenomenon has been maintained. When the diameter of the nanopore is 4nm, the peak ion concentration drops to 1.6 times the bulk value. The results in the figure show that the nanopore size constraints effect begins to transition to bulk behavior at the nanopore diameter of 3nm.

Figure 4. The ratio of the pore concentration to the body concentration as a function of nanopore diameter. When the diameter of the nanopore is less than 2-nm, the size constraint effect is more obvious

3.3 The influence of concentration polarization on ion transport

In a cylindrical pore, we can also simply express the conductance as $G = \kappa \left(\frac{L}{\pi R^2} + \frac{1}{2R} \right)^{-1}$, where G and κ are the conductance and conductivity of an electrolyte inside the pore, respectively; R and L are the radius and the length of a nanopore, respectively. The conductivity can be written as $\kappa = \sum_i F n_i \mu_i$, where n_i and μ_i are the concentration and the electrophoretic mobility of an ion of the i th specie, respectively; e is the Faraday constant. Various power-law relations between the conductance and ion concentration ($G \propto n_0^\alpha$) have been widely studied^{22,25}. Therefore, ion concentration polarization is an important determinant of the access conductance. When the ionic bulk concentration increased from 0.5 M to 2.5 M, the number density peak of the concentration polarization region also increased, with Cl⁻ from 1.15 nm⁻³ to 2.67 nm⁻³, and Na⁺ from 0.97 nm⁻³ to 2.22 nm⁻³. Concentration polarization is the result of the combined action of ions driven by an electric field and the selectivity of nanopores to ions. When the electric field intensity remains unchanged, the body ion concentration increases, the electric potential on both sides of the film basically remains unchanged, and the depletion effect of the concentration polarization region increases. In order to maintain the potential difference between the two ends of the nanopore, the enrichment effect must also be increased, and the two reach a dynamic equilibrium as the concentration increases.

Figure 5. Ion number density as a function of bulk ion concentration.

4 Conclusions

This paper uses molecular dynamics technology to simulate the ion concentration polarization phenomenon in graphene nanopores with different electric field strengths, different nanopore diameters, and different salt solution concentrations. The research has a deeper understanding of the nature of ion transport in nanopores. The greater the electric field strength, the greater the ion number density in the ion concentration polarization region, and the weaker the ion concentration polarization phenomenon is when the electric field strength is small. In nanopores of different pore diameters, the ion polarization properties are also different. The smaller the pore diameter, the stronger the selectivity of the nanopore to ions, the more difficult it is for ions to enter the pore, and the more obvious the ion polarization phenomenon. When the salt solution concentration is different, the numerical density peak value of the ion polarization area will increase with the increase of the ion body concentration. However, the increase in body concentration remained basically unchanged. These conclusions may help a new understanding of the design of nanofluidic devices.

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