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Transport of salty water through graphene bilayer in an electric field: A molecular dynamics study

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ABSTRACT

Molecular dynamics simulations are carried out to study the pressure-driven transport of salty (NaCl) water through the nanochannels formed by a graphene (GE) bilayer with and without a vertical electric field. The simulation results show that the channel thickness influences not only the velocity and numbers of water molecules and ions inside the channel, but also their responses to varied pressure and electric field intensity. The salt rejection rate is characterized by considering both the numbers of ions and water molecules inside the channel and their velocities. When the electric field is not imposed, the salt rejection rate varies slightly in the high-pressure range (50–300 MPa), and is mainly affected by the channel thickness. When an electric field with high intensity (1–5 V/Å) is imposed vertically under high driving pressure (300 MPa), ions can be trapped inside the nanochannel. Simulations under lower electric field (0.01–0.1 V/Å and 0.05–0.2 V/Å) and pressure (5 MPa and 10 MPa) are also conducted. Under these circumstances, GE nanochannels can reject ions from entering the channel, indicating improved salt rejection rate and reduced ion channel accumulation.

1. Introduction

Graphene (GE) has recently attracted substantial attention in water desalination techniques [1–8]. Reverse osmosis (RO) membranes derived from GE have been reported to show advantages over conventional RO membranes because of ultimate thinness, high mechanical strength, and more importantly, high water permeability [2–5,9–11]. GE derived membranes can be fabricated by stacking functionalized GE nanosheets, where nanochannel and nanopores are formed. Interlayer distance of graphene oxide (GO) membrane can be less than 0.7 nm if made by vacuum filtration in the dry state, enabling water molecules to permeate through while blocking hydrated ions and other target molecules [5,3,12]. Confined in the nanostructures, water still shows high permeability through GO membranes. This is attributed to the capillary network formed by the pristine GE domains, where water can flow almost frictionlessly [5,11].

GE-based membranes also have superior energy efficiency compared with other RO technology [13]. Meanwhile, functionalized GO can enhance the hydrophilicity of the membrane and provide negative charges, and thus possessing anti-fouling properties [14]. However, the scale-up ability remains a critical issue for the mass production of GE-based membranes. Many studies have reported on various possible fabrication approaches, such as chemical vapour deposition and subsequent transfer to substrates [15], restacking GO flakes by filtration on a back support [2], etc. Most of these methods suffer from scalability issues. Recently, Akbari et al. developed a method to produce large-area, highly ordered, and multi-layered GE-based films by making use of the shear alignment of discotic nematic GO fluid [16]. This scalable method brings hope to the mass production of GE-based membranes for industrial applications.

Molecular dynamics (MD) simulation has been used to investigate the transport of salty water through GE nanopores and nanochannels [4,11,17–24]. GE single layer with nanopores bonded with chemical functional groups at the pore ring can limit the salt passage depending on the pore size, functional groups and applied pressure or electric field [18–22]. Cohen-Tanugi et al. also carried out MD simulations of salty water passing through multilayer nanoporous GE with different interlayer width as well

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as pore offset, and demonstrated that salt separation performance can be manipulated by different multilayer design [17]. Simulation results also showed that the water molecules display layered structure inside GE nanochannels which affects the water flow rate significantly [4,8]. GE nanochannels with the thickness of allowing one monolayer of water molecules passing through do not allow ions inside [4]. However, a systematic study of ion transport through the nanochannel formed by GE bilayers, especially the interaction of ions with water molecules and GE, is still needed to provide further guidance on the design and application of GE-based RO membranes.

High surface area and excellent conductivity also make GE feasible for the fabrication of electrodes in capacitive deionization (CDI) [1,8,26,27]. The experimental results from these studies showed that the electrosorption capacity of GE-derived electrodes can be enhanced by mixing GE with other chemicals or creating specific structures. In CDI, salty water flows between the electrodes [26,27]. MD simulations can provide insights into the effect of nanostructure on CDI performance which is still not fully determined or optimized [28]. The present work focuses on the behavior of ions and water molecules in flowing solutions rather than static solutions, while studies so far often use the latter one for MD simulations due to their relative ease to be set up [25,29]. Nasrabadi and Foroutan carried out MD simulations to demonstrate that carbon nanotube (CNT) electrodes are suitable for ion separation by investigating the atomic interaction among ions, water molecules and CNT [25]. However, the feasibility study of GE derived electrodes is mostly based on material characterization and experiments so far.

The present study is targeted at a systematic investigation of the transport of salty water through the nanochannel formed by a GE bilayer with different channel thickness, applied pressure as well as external electric field using MD simulations. Interactions among the ions, water molecules and GE are also investigated. The simulation results provide useful guidelines for the design and application of GE-derived material for RO or CDI desalination.

2. Simulation details

The studied system consists of a nanochannel formed by the bilayer GE and two water reservoirs at each end of the channel constrained by GE walls, as shown in Fig. 1. The left-hand feeding reservoir is initially filled with salty water containing 16 Na^+ and 16 Cl^- dissolved with 922 water molecules, and the right-hand receiving reservoir with pure water containing 954 water molecules. The salinity in the feeding reservoir is 4.86 g/L, slightly higher than sea water salinity (3.5 g/L). Both reservoirs have the same dimension of $40 \times 20 \times 40$ Å^3. The GE bilayer is parallel to the *xy* plane with a constant length L 32 Å, while its thickness d varies from 7 to 20 Å. The GE constrain walls are set normal to the bilayer plane to restrict water and ion movement.

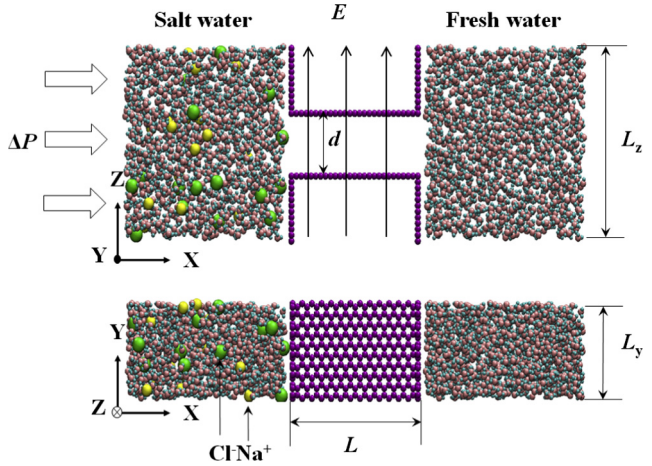

Fig. 1. Front and top view of the simulated system consisting of two reservoirs and a nanochannel formed by the GE bilayer. At the initial condition, the left-hand reservoir is filled with salt (Na^+ and Cl^-) water, and the right-hand reservoir is filled with pure water. The two reservoirs are separated by GE nanochannel and constrain wall.

Simulations are carried out using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [30]. Boundary conditions are set as periodic in all three dimensions to maintain the continuous feeding. The Transferable Intermolecular Potential 3P (TIT3P) [31] is applied to model the water molecules, and partial charges of O and H are −0.834e and 0.417e. Other atomic interactions are modelled using CHARMM force field [32], including Coulombics and van der Waals (vdW) interactions. The long-range Coulombics are computed with the particle-particle-particle-mesh (PPPM) method with a cutoff of 12 Å, and vdW interaction is modelled using Lennard-Jones (LJ) potential with a cutoff at 10 Å. LJ parameters and charges of each atom species are summarized in Table 1 according to previous research studies [23,32,33]. The LJ pair parameters between species i and j are calculated using the Lorentz-Berthelot combining rules except for C-O and C-H interactions. The energy well ε and zero-across distance σ between C and O are set as 0.0937 kcal/mol and 3.19 Å, while ε and σ between C and H are all set as 0 [23].

The NVT ensemble with a Nosé-hoover thermostat is used to keep the temperature at 300 K. The GE nanochannel and constrain walls are treated as rigid body with carbon atoms fixed. The SHAKE algorithm is used to constrain the bond and angle of water molecules to maintain the rigid molecule structure. After all the water molecules are relaxed for 50 ps with a timestep of 0.5 fs to reach equilibrium state, a pressure difference ΔP is applied by adding a force f on all the O atoms in the left feeding reservoir along the positive X-direction. The force f is calculated as [23]

$$f = \Delta P L_y L_z / n \tag{1}$$

where n is the number of water molecules in the left water reservoir, and L_yL_z is the cross-section area shown in Fig. 1. Our simulations focus on the pressure difference ΔP ranging from 50 to 300 MPa to obtain data for statistical calculations. The external electric field is added in the channel region and vertical to the *xy* plane. Because ions and water molecules move very fast due to the high pressure, the applied electric field E also has a large intensity (1–5 V/Å) to obtain distinguishable results. The intensity range here is with the same magnitude of electric field that can break bonds and induce ionization of water molecules [34], but the rigid structure of water molecules is kept using the SHAKE algorithm. Cases with lower pressures (5 MPa and 10 MPa) and lower electric field intensities (0.01–0.1 V/Å and 0.05–0.20 V/Å) are also tested, which are discussed in Section 3.3. The simulated system can reach the steady state within around 100 ps with the imposed force f and electric field E. The simulation is then carried on for another 1.5 ns (2.5 ns when ΔP = 5 and 10 MPa) to collect data.

Table 1
LJ parameters and charges used in the simulation.

Species	ε (kcal/mol)	σ (Å)	q (e)
H	0.0461	0.40	0.417
O	0.1521	3.15	−0.834
C	0.0700	3.98	0
Na^+	0.0874	2.74	1
Cl^-	0.0356	5.03	−1