1 Introduction

In recent years, ion transport through membranes with nanosized pores or channels has become a rapidly growing research field. For example, ion transport through cell membranes via ion channels is a key process in biology.1 Ion transport through semipermeable membranes is widely used in desalination,2–5 nanofiltration6–9 and nano-fluids.10–15 In general, the transport behavior is mainly affected by electrostatic interactions, steric exclusion of the hydration shell and coordination with the solvent or functional group at the pore edges, where the size of the pore or channel in the membrane plays a key role. For example, K+ and Cl− (their hydrated diameters are about 0.66 nm) cannot be transported through a neutral charged graphene nanopore with a diameter of 0.4 nm, but they can cross a graphene nanopore with a diameter of 0.8 nm.16 Nevertheless, if the pore is functionalized with a charged or partially charged functional group, the critical size of the pore can be changed (for ion transport). For example, Král et al.17 reported that a 0.5 nm-diameter graphene nanopore functionalized with F− atoms allowed the transport of ions (Li+, Na+ and K+), due to the fact that the charged nanopore could reduce the transport energy barrier of ions carrying the opposite charge.

As mentioned before, graphene is one of the most widely used 2D membranes for ion transport.27–28 In addition to graphene membranes, other materials (e.g., TiO2,29 silica30 and MoS2,31) can also be used as membranes for ion transport. However, these two-dimensional materials encounter the same limitations, namely, they must have some pre-treatment for real applications because they do not have inherent nanopores for mass transport. Despite the rapid development of nanotechnology, it is still difficult to fabricate nanopores with a proper shape and size for ion selectivity at present. Additionally, to resolve the trade-off between selectivity and permeability, the membrane generally needs a high density of nanopores.32

As new 2D materials, C2N membranes have recently attracted great attention,33–35 and possess intrinsic regular and uniformly distributed nanopores with subnanometer diameters, and have an extremely high thermal stability and a tunable wide band gap.36–38 Thus, they may have inherent advantages for different molecules with different sizes. For example, a strained C2N membrane can serve as a filter for highly efficient water desalination. It has been found that only water from seawater can permeate the C2N membrane, their flux is strengthened by one to four orders of magnitude relative to that of other membranes and the transport behavior can be precisely controlled with tensile strain.39–40 Additionally, C2N membranes also possess excellent capability for gas separation. Liu et al.41 showed that C2N membranes exhibit remarkable selectivity for H2 from among other atmospheric gases. Xing et al.42 reported that C2N membranes exhibit an exceptional ability to separate He from natural gas with a high permeability (1 × 107 GPU) for He at room
temperature. Although great progress has been made on water and gas separation using C2N membranes, to the best of our knowledge, there has still been no attempt to use a C2N membrane for ion transport and selectivity, which may hinder its wider application in nanotechnology.

In this work, we mainly focus on the transport of ions (i.e., Li\(^+\), Na\(^+\), K\(^+\)) through a C2N membrane using all-atom molecular dynamic (MD) simulations. As we will show below, the monolayer C2N membrane exhibits higher ionic permeability (compared to that of graphene) and excellent ion selectivity under a low electric field. The underlying mechanism of the ion selectivity will be discussed in detail. Furthermore, the effect of the layer number of the C2N membrane on the ion transport and electroosmosis will also be investigated.

2 Methods

As shown in Fig. 1a, our simulation system contained one C2N membrane, water molecules and ions (Li\(^+\), Na\(^+\), K\(^+\) and Cl\(^-\)) through a C2N membrane using all-atom molecular dynamic (MD) simulations. As we will show below, the monolayer C2N membrane exhibits higher ionic permeability (compared to that of graphene) and excellent ion selectivity under a low electric field. The underlying mechanism of the ion selectivity will be discussed in detail. Furthermore, the effect of the layer number of the C2N membrane on the ion transport and electroosmosis will also be investigated.

Fig. 1 Schematic illustration of ion transport through a C2N membrane. (a) An electric field along the z-axis drives ion transport through the C2N membrane. For clarity, water molecules in the simulation box are not displayed. (b) The atomic structure of the C2N monolayer, bilayer and trilayer membranes; the C and N atoms are depicted as cyan and blue spheres, respectively; the initial stacking of the multilayer C2N membrane was A–B–C.

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The number of passed ions as a function of time under an electric field of 0.1 V nm⁻¹ and 0.5 V nm⁻¹ (Fig. 2a). As expected, with an increase in electric field, the currents of each ion nonlinearly increase due to the accelerated dehydration of the cation shell under the higher electric field. Notably, the current of the K⁺ ion through a single nanopore in the C₂N membrane is about 1.16/30 = 0.039 nA under E = 0.15 V nm⁻¹, where 30 is the number of nanopores in the C₂N membrane. It is approximately the same as that from a single pore in a graphene membrane (0.032 nA) under the same conditions. However, the density of nanopores in the C₂N membrane (~10¹⁴ cm⁻²) is two orders greater in magnitude than that in the graphene membrane (~10¹² cm⁻²). As a result, the ion permeability of the monolayer C₂N membrane is much larger than that of the graphene membrane. Moreover, Fig. 2b also shows that the ions with smaller hydrated diameters (the Li⁺ hydrated diameter is 0.76 nm, the Na⁺ hydrated diameter is 0.72 nm and the K⁺ hydrated diameter is 0.66 nm) have larger currents under the same electric field. However, this trend does not appear under an electric field of 0.25 V nm⁻¹ to 0.4 V nm⁻¹ (see the inset in Fig. 2b).

To better compare the performance of the membrane in applications such as ion separation, the ionic permeability ratio (defined as the ratio of the number of passed ions to the number of passed Li⁺ ions) under different electric fields was then calculated (Fig. 2c). It was found that the ratio of K⁺ and Na⁺ relative to Li⁺ was very high when the electric field was low. Then it rapidly decreased, before increasing gradually and then finally reaching equilibrium as the electric field went on increasing. A similar phenomenon was also observed in the 1:1 binary K⁺/Li⁺ mixed solution with the total concentrations of 0.5 M, 1.0 M and 1.5 M (see the dashed line in Fig. 2c). In addition, very little difference existed between the three mixed solutions, which also indicates that the concentration of ions may have little influence on the ion selectivity. The ratio of K⁺ relative to Na⁺ (as a function of the electric field) was nearly identical to that of K⁺ relative to Li⁺ (see inset in Fig. 2c), which is consistent with that observed in the case of the graphene nanopore functionalized with carbonyl groups. Generally, the C₂N membrane exhibits excellent ion selectivity, especially under a low electric field. The ions with smaller hydrated diameters generally have higher selectivity under the same electric field for the monolayer C₂N membrane, in line with other membranes. In all the simulations, we found that the Cl⁻ ion could not pass through the monolayer C₂N membrane because the N atoms (carrying negative charges, −0.48 e) were around the nanopores of the membrane. These negatively charged atoms can prevent the transport of Cl⁻ ions, indicating that the monolayer C₂N membrane exhibits cation selectivity.

To study the underlying mechanism of the ion selectivity, the potential of mean force (PMF) of a single ion being transported through the monolayer C₂N membrane (in the absence of an electric field) was calculated (see Fig. 3a). Taking the Li⁺ ion as an example, when it approaches the C₂N membrane, due to the deformation of the hydration shell, the PMF firstly increases slowly. As it goes on approaching membrane, the PMF will then decrease a bit and reach a minimum at z = −0.36 nm, which is mainly attributed to the attraction interaction between the cation and the negatively charged nanopore (i.e., N atom). With the further decrease in z, due to the dehydration of the ion (the coordination number of ions with water molecules begins to decrease, see Fig. 3b), the PMF will again increase, and reach a maximum when z is about −0.12 nm (see the blue circles in Fig. 3a). Nevertheless, when the ion and the pore are very close, the electrostatic interaction becomes very large, and could be much larger than the dehydration-induced exclusion interaction. Hence, the PMF will again decrease and reach a minimum when z = 0 nm (see the blue rectangles in Fig. 3a). To better discuss the position distribution in the following sections, we define the region between the center of the C₂N membrane (solid line) and the maximum (dotted line) in the PMF as the attraction region, and the region between the minimum (dashed line) and the maximum (dotted line) in the PMF as the repulsion region (see Fig. 3a). Similar phenomena were also observed in the case of Na⁺ and K⁺ ions although the values for the energy barrier/well and the corresponding z coordinates
Na\(^{+}\) ions are mainly located at \(z = -0.48\) nm and \(z = -0.22\) nm, partly in the repulsion region and partly in the attraction region. As a result, there are more chances for a Na\(^{+}\) ion passing through the membrane (compared to those for a Li\(^{+}\) ion). Moreover, due to their lower hydration energy, the K\(^{+}\) ions are mainly located around the attraction region \((\Delta E = -0.27\) nm), where the ions can have their translocation facilitated. Under a low electric field, since the ions are mainly distributed far away from the pores (see Fig. 4b), the probability of ion transport should be much lower (when compared to that under a high electric field). In particular, as previously mentioned, the Li\(^{+}\) ion has the highest energy barrier and a low external field can hardly drive the Li\(^{+}\) ion through the pore (the position distribution of a Li\(^{+}\) ion inside the nanopore is nearly zero). Meanwhile, for a Na\(^{+}\) ion, a peak in the number density profile appears at \(z = 0\) nm, indicating that the dwell time of a Na\(^{+}\) ion is elongated; for a K\(^{+}\) ion, a peak appears at the exit of the nanopore \((\Delta E = 0.13\) nm), meaning that the number of passed K\(^{+}\) ions has increased. These lead to a more obvious difference between the transport ability of the three ions at \(E = 0.1 \text{ V nm}^{-1}\). In the case of \(E = 0.3 \text{ V nm}^{-1}\), it was found that the three types of ion are mainly distributed in the repulsion region, and their distribution inside the nanopore is mostly the same (see Fig. 4c). Thus no obvious difference between the transport ability of the three ions occurs under this electric field.

3.2 Ion transport through the multilayer C\(_2\)N membrane driven by an electric field

Previous reports have shown that multilayer membranes possess higher ion selectivity, attributed to the extension of the selection region.\(^{23}\) Here, the translocation of ions through the multilayer C\(_2\)N membrane was also investigated under the electric field \(E = 1.0 \text{ V nm}^{-1}\). As shown in the inset in Fig. 5a, it was found that ions with smaller hydrated diameters have larger passing rates regardless of the layer number. It also shows that the number of passed ions decreases with the increase in the number of layers. Additionally, the ionic selectivity for the monolayer C\(_2\)N membrane is larger than that for the multilayer C\(_2\)N membrane (see Fig. 5a). This means that increasing the number of layers cannot increase the ion selectivity for the C\(_2\)N membrane, which seems to contradict the results from the graphene membrane.\(^{23}\)

To provide a possible explanation for the above results, typical snapshots of an ion passing through the C\(_2\)N membranes are shown in Fig. 5b. Due to the electrostatic interactions and van der Waals interactions, the multilayer C\(_2\)N membrane shows the A–B–C stacking mode,\(^{28}\) which is different from the aligned stacking mode in the graphene membrane. This unique stacking mode causes a decrease in the effective area of the pores (see Fig. 5b). Meanwhile, increasing the number of layers leads to an increase in channel length and roughness in the interior surface of the pores. As a result, the transport time of the ions through the membrane increases. As shown in Fig. 5b, K\(^{+}\) ions stay longer in the region between the adjacent C\(_2\)N sheets when passing through the trilayer C\(_2\)N membrane. This means that the ion passing rate in the case of
the multilayer membrane is lower than that in the monolayer membrane. Additionally, the K⁺ ion has a larger size compared to that of the Na⁺ ion and Li⁺ ion (the ionic radii of K⁺, Na⁺ and Li⁺ are 0.133 nm, 0.095 nm, 0.06 nm, respectively), resulting in a larger resistance. Thus, the K⁺ ion has a larger decrement. To summarize, the decreased ion passing rate in thick C₂N membranes mainly originates from the increase in the length of the channels and the decrease in the effective area of the pores.

3.3 Electroosmosis induced by ion transport

The ion flow (through nanopores) driven by the electric field can lead to electroosmosis. To describe the electroosmotic flow, the mean number of passed water molecules (in the ionic hydration shell) induced by one passed ion (i.e., \( N_{\text{water}}/N_{\text{ion}} \)) was computed. As can be seen from Fig. 6a, the ratios of three types of ion for the monolayer C₂N membrane are all larger than 1, while the ratios for the multilayer C₂N membrane are all smaller than 1, indicating that the ion capability for dragging and pushing water is reduced with an increase in layer number. In addition, in the case of the monolayer C₂N membrane, smaller ions (with larger hydrated diameters) have a stronger capability for electroosmosis, which is consistent with the results with graphene functionalized by F⁻-N atoms. To further analyze the electroosmosis, typical snapshots of the transport process were taken. As shown in Fig. 6b, two water molecules distributed at both sides of the ions can be pushed and dragged by the Li⁺ ions, resulting in the permeation of both the ions and the water molecules through the monolayer membrane. In contrast, when the size of the ion increases, the partial water molecules around the K⁺ ion can be dragged (see Fig. 6c), leading to a smaller number of passed water molecules.

In the case of the multilayer C₂N membrane, ions of a smaller size drag fewer water molecules through the bilayer and trilayer C₂N membranes. These results are the opposite to those with the monolayer C₂N membrane. As a Li⁺ ion passes through the bilayer C₂N membrane, due to its small size the relative position between the Li⁺ ion and the pushed water molecules can be adjusted inside the interlamination of the membrane (the line connecting the ion and the water molecule changes from perpendicular to parallel to the plane of the membrane, see Fig. 6d). As a result, the pushed water molecules will be stripped away from the ion when the Li⁺ ion further penetrates through the nanopore of the second layer. Thus, water...
molecules can hardly pass through the nanopore along with Li$^+$ ions under these circumstances. On the other hand, with the increased ion size, the relative position of the water molecules and the K$^+$ ion cannot be adjusted inside the interlamination of the membrane (see Fig. 6e). Consequently, the pushed water molecule will not be stripped away from the K$^+$ ion when the ion goes on passing through the second layer, and can permeate the nanopore along with the ions. In general, the electroosmosis flow of the multilayer C$_2$N membrane is smaller than that of the monolayer C$_2$N membrane, but the multilayer C$_2$N membrane may be well-suited as a cathode material for water desalination using an electroosmotic flow (the removal of ions from saline solution$^{13}$).

4 Conclusion

In summary, three types of ion transport through C$_2$N membranes under an electric field have been investigated using all-atom molecular dynamics simulations. When the ions pass through a monolayer C$_2$N membrane, the ionic current nonlinearly increases with the electric field, and the current is larger than that in the case of a graphene membrane, which is mainly due to its higher density of nanopores. Moreover, it was found that the monolayer C$_2$N membrane presents excellent ion selectivity (especially under a low electric field) due to the distinct dehydration ability of different ions and the interactions between the ions and the pore edges. In addition, the effect of the layer number of the C$_2$N membrane on the ion transport was also studied. Interestingly, the multilayer C$_2$N membrane showed the weaker ion selectivity, but has potential for desalination. Overall, this work can help us better understand the underlying mechanism of the transport of ions through a charged nanopore, and may shed light on the design of C$_2$N membrane based nanodevices in real applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 21604060, 11474155, 11874045 and 11774147). We are grateful to the High Performance Computing Center (HPCC) of Nanjing University for doing the numerical calculations in this paper on its blade cluster system.

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