Analysis of Potential Barrier for Ionic Transport through Si3N4 Nanopores

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ABSTRACT

Potential barrier plays a key role in ionic transport through nanoporous membranes. We numerically study the contribution of the potential barrier to the ionic current through a cylindrical Si3N4 nanopore using molecular dynamics simulations. We extract the height of the potential barrier from the best fit using a simple polynomial model of the ionic current. We reveal that the surface atoms make a contribution to the potential barrier. This study provides the height of the potential barrier so that it is valuable information about the underlying mechanism of ionic transport through nanopores.

1. Introduction

Ionic transport through nanopores has significant potential for applications in ionic circuits,1 ion sieves,2 biosensors,3 desalination,4 and energy conversion.5 These devices exploit the ability to tune permeation properties of ions through nanopores; hence, the permeation properties of ions have been investigated by many researchers.6–9 An important example is the ion pump,7,8 which is used for transporting ions against their concentration gradient. Ion pumping is caused by the periodic shifting of electrostatic potential.7 It has been reported that apertures with charged surfaces lead to permselectivity due to the electrostatic exclusion of co-ions and enrichment of counternions resulting from electrostatic interactions.9 Electric double-layer supercapacitors can store electrical energy in the interface between an electrolyte and a solid electrode.10,11 Especially, electro-chemical capacitors, which is an important application example of nanopores, have emerged as promising devices for energy storage,12 which are described by the parameters

\[ f(T) = \frac{z e_0 n_p k T \sigma c}{h \left( e^{\frac{e_0 V}{k T}} + e^{-\frac{e_0 V}{k T}} \right)} \left( 1 - \exp \left( -\frac{e_0 V}{k T} \right) \right) \]

where \( z \) is the valence number, \( e_0 \) is the elementary charge, \( \sigma \) is the cross-sectional area of the pore, \( I \) is the distance between the interior and the exterior of the nanoporous membrane, which plays a key role in ionic transport through the nanopore, needs to be further investigated.

In this study, we used molecular dynamics (MD) simulations to investigate the contribution of potential barrier to the ionic current through a cylindrical Si3N4 nanopore. We introduced a first-degree polynomial model to describe the energy profile of the nanopore. We examined the current behavior with respect to the membrane thickness, radius of the nanopore, and bias voltage in order to elucidate their effects on the potential barrier at the pore aperture.

2. Method

To analyze the ionic transport through a nanopore, we considered a Si3N4 membrane with nanopores. Throughout the analysis, we aimed to reveal the potential barrier at the interface between the solution and the membrane. In this section, we first introduce a theoretical model to describe the potential barrier. Second, we present the setup of the MD simulation.

2.1 Analytical model for ionic transport through nanopores

We used the following approach to calculate the potential barrier. There are potential barriers at the interface between the solution and the membrane which affect ionic transport. Figure 1(a) shows the schematic depiction of the potential curve in the vicinity of the nanopore. The interface between the interior and the exterior of the membrane is theoretically represented as a sequence of energy barriers. Then, the ionic current \( I \) is described as follows:13

\[ I \approx a(f_1) T + I_0, \]

where \( a(f_1) \) and \( f_1 \) are determined by the structure, molecule of the membrane, and external bias voltage.

From Eq. (1), assuming that \( \exp(-e_0 V/kT) \ll 1 \) and \( f_1 = f_2 \), we can express the ionic current as a first-degree polynomial of temperature \( T \):

\[ I \approx a(f_1) T + I_0, \]

\[ a(f_1) \equiv \frac{z e_0 n_p k T c}{2 h e^{e_0 V/k T}}. \]
where \( I_0 \) is the \( f \)-intercept. The value of the slope \( a(f_i) \) depends on the potential barrier \( f_i \). Thus, the potential barrier is a key parameter that affects the ionic transport through nanoporous membranes. We should emphasize that the heights of the potential barrier, \( f_i \), is associated with the external voltage \( V \). Thus, the current \( I \) is the function of \( V \) and \( T \). The MD simulation results allow us to plot the best fit using Eq. (2). We can then extract the value of the potential barrier \( f_i \).

Note that our assumption, \( f_1 = f_2 \), means that the potential barriers have same height at the both apertures. Moreover, for a numerical example, we have \( \exp(-e_0V/kT) = 6.82 \times 10^{-10} \) using \( e_0 = 1.60 \times 10^{-19} \) C, \( z = 1 \), \( V = 0.5 \) V, \( k = 1.38 \times 10^{-23} \) J/K, and \( T = 275 \) K. Thus, our assumption, \( \exp(-e_0V/kT) \sim 1 \), is reasonable in the analysis.

2.2 Numerical simulation setup

The system setup of the nanopore considered in this study is shown in Fig. 1(b). The system consists of a Si3N4 membrane immersed in a water solution of sodium and chlorine ions. Silicon nitride has a layered structure in the \( z \) direction. A cylindrical nanopore of radius \( r \) was drilled through the center of the membrane. An external electric field \( E = V/d \) was applied along the \( x \) direction, where \( V \) is the bias voltage across the simulation cell region of length \( d = 90 \) nm. The temperature was varied from 275 to 318 K. The different thicknesses of the membrane, radii of the nanopore, and bias voltages used for the MD simulations are listed in Table 1.

The ionic transport was studied using the all-atom MD code NAMD2,14 The ion concentration was set to 1 mol L^{-1}. Periodic boundary conditions were employed in the directions perpendicular and parallel to the membrane. A CHARMM27 force field was used for the simulations. The Si3N4 atoms were confined to mimic the dielectric properties of Si3N4, and a time step of 1 fs was used for all the simulations. The temperature was maintained (at the examined value) using a Langevin dampening parameter of 0.2 ps^{-1} in the equations of motion. The Van der Waals interactions were gradually cut off until reaching zero in the range of 10 to 12 Å. The energy was initially minimized for 3 ps and then equilibrated for 100 ps at zero electric field. Subsequently, the simulations were carried out for 15 ns in the NTV ensemble. The first 5 ns were used as relaxation time for the system to reach a steady state, and the remaining 10 ns were used in the analysis.

3. Results and Discussion

The ionic current is represented as the rate at which charge flows through the membrane. This was calculated using the trajectories of the ions in the MD simulation results:

\[
I = \frac{dQ}{dt} = \frac{(N_\text{p} + N_\text{n})e_0}{\tau},
\]

where \( Q \) is the charge flows, \( \tau \) is the time period, \( N_\text{p} \) and \( N_\text{n} \) are the numbers of transported anions and cations per the time period, respectively. From the MD simulation results, we counted the number of ions transporting over the plane at center of the membrane, see Fig. 1(b).

Figure 2 shows the temperature dependences of the current at different simulation setups. To study the behavior of ion transport through nanopores, we varied the thickness of the membrane (setting A), radius of the nanopore (setting B), and bias voltage (setting C) as shown in Table 1. The values of the other parameters were the same for each setup. Figures 2(a)–2(c) demonstrate that the current increases with the temperature. This is because the transition rate of the ions from the pore exterior (or interior) to the interior (or exterior) is proportional to the temperature. Specifically, the current–temperature dependence is approximately linear. The best fits obtained using Eq. (2) are shown as dashed lines in Fig.

Table 1. Varied parameters in this study.

| Parameter      | Setting A                  | Setting B                  | Setting C                  |
|----------------|----------------------------|----------------------------|----------------------------|
| Thickness (nm) | 0.58, 1.16, 1.75, 2.33, and 2.91 | 1.16                       | 1.16                       |
| Radius (nm)    | 3                          | 1, 1.5, 2, 2.5, and 3      | 3                          |
| Bias voltage (V)| 0.5                       | 0.5                        | 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 |
Comparing the numerical results and the best fits, it can be inferred that the model in Eq. (2) successfully replicates the ionic current in the narrow straight nanopores and captures the underlying dynamics of ionic transport.

We observed that the current changed significantly owing to the structure of the nanopore. To understand this phenomenon, we investigated the height of the potential barrier $f_1$. Figure 3 shows the height of the potential barrier extracted from the best fit in Eq. (2). Interestingly, the height of the potential barrier linearly increases with the pore length, as shown in Fig. 3(a). The ion trapping inside the nanopore owing to ion–ion and ion–wall interactions impedes the flow of the transporting ions. This current suppression indicates that long pores increase the potential barrier. Thus, the pore length contributes significantly to the potential barrier. It should be noted that the amount of current decreases with increase in the pore length, as shown in Fig. 2(a).

From Fig. 3(b), the pore of $r = 1$ nm provides a high potential barrier owing to local electric fields created by the atoms at the pore entrance. When the pore radius is narrow, the diffusive behavior is reduced at the interface between the interior and the exterior of the pore owing to the strong interaction between the ions and surface atoms. Consequently, a narrow pore leads to an infrequent transition over the interface. For $r \geq 1.5$ nm, we observe an almost flat slope in Fig. 3(b). The wide pore does not affect the potential barrier significantly because the surface atoms at the pore aperture make a minor contribution to the ionic current.

As shown in Fig. 3(c), the potential barrier decreases with increase in the external bias voltage. Generally, the transition rate is enhanced at higher bias voltages owing to the extra drift energy supplied by the electric field. This means that the height of the potential barrier decreases at higher bias voltages. Thus, our numerical analyses provide reasonable results for the investigation of ionic transportation through nanopores.

4. Conclusion

We analyzed the potential barrier at the interface between NaCl solution and nanoporous Si$_3$N$_4$ membrane using MD simulations. We demonstrate that the surface atoms at the pore aperture significantly affect the potential barrier because they exhibit strong electrostatic interactions with the transporting ions. Moreover, the surface atoms of the pore interior contribute to the potential barrier. The results of the present study are useful for understanding the underlying mechanism of ionic transport through nanopores.
Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.21-00059.

References

1. R. A. Lucas and Z. S. Siwy, ACS Appl. Mater. Interfaces, 12, 56622 (2020).
2. J. Lu, H. Zhang, J. Hou, X. Li, X. Hu, Y. Hu, C. D. Easton, Q. Li, C. Sun, A. W. Thornton, M. R. Hill, X. Zhang, G. Jiang, J. Z. Liu, A. J. Hill, B. D. Freeman, L. Jiang, and H. Wang, Nat. Mater., 19, 767 (2020).
3. I. Vlassiouk, T. R. Kozel, and Z. S. Siwy, J. Am. Chem. Soc., 131, 8211 (2009).
4. B. R. Putra, E. Madrid, L. Tshwenya, O. A. Arotiba, and F. Marken, Desalination, 480, 114351 (2020).
5. C.-Y. Lin, C. Combs, Y.-S. Su, L.-H. Yeh, and Z. S. Siwy, J. Am. Chem. Soc., 141, 3691 (2019).
6. L. Bocquet and E. Charlaixa, Chem. Soc. Rev., 39, 1073 (2010).
7. Z. Siwy and A. Fulinski, Phys. Rev. Lett., 89, 198103 (2002).
8. D. M. Huang, C. Cottin-Bizonne, C. Ybert, and L. Bocquet, Phys. Rev. Lett., 101, 064503 (2008).
9. A. Plecis, R. B. Schoch, and P. Renaud, Nano Lett., 5, 1147 (2005).
10. P. Sharma and T. S. Bhatti, Energy Convers. Manage., 51, 2901 (2010).
11. Y. Okada, T. Ito, T. Minamikawa, H. Kamisuki, S. Higai, and K. Shiratsuyu, Electrochemistry, 81, 808 (2013).
12. H. Yamamoto, K. Iwamoto, K. Matsumoto, and R. Hagiwara, Electrochemistry, 89, 118 (2021).
13. P. Läuger, Biochim. Biophys. Acta, 311, 423 (1973).
14. J. C. Phillips, R. Braun, W. Wang, J. Gumbart, E. Tajkhorshid, E. Villa, C. Chipot, R. D. Skeel, L. Kale, and K. Schulten, J. Comput. Chem., 26, 1781 (2005).