Original Research

An equivalent 1D nanochannel model to describe ion transport in multilayered graphene membranes

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ABSTRACT

Multilayered graphene-based membranes are promising for a variety of applications related to ion or molecule transport, such as energy storage and water treatment. However, the complex three-dimensional cascading nanoslit-like structure embedded in the membrane makes it difficult to interpret and rationalize experimental results, quantitatively compare with the traditional membrane systems, and quantitatively design new membrane structures. In this paper, systematic numerical simulations were performed to establish an equivalent one-dimensional (1D) nanochannel model to represent the structure of multilayered graphene membranes. We have established a quantitative relationship between effective diffusion length L_eff and cross-section area A_eff of the 1D model and our recently developed two dimensional (2D) representative microstructure for graphene membranes. We find that only in the cases of a relatively large lateral size L (> ~100 nm) and a small slit size h (< 2 nm), the effective diffusion length L_eff and A_eff can be calculated by an over-simplified but often used model. Otherwise, they show complex dependence on all three structural parameters of the 2D structural model. Our equivalent 1D nano-channel model can reproduce experimental results very well except for h < 0.5 nm. The discrepancy could be attributed to the anomalous behaviour of molecules under nano-confinement that is not considered in our simulations. This model can also be extended to multilayered membranes assembled by other 2D materials.

1. Introduction

Recent research has shown that a new class of multilayered membranes assembled by 2D materials such as graphene and graphene oxide [1,2] hold great promise for use in supercapacitors [3–5], catalysis [6,7], batteries [8–10] and water desalination [11–14]. With a unique cascading nanoslit microstructure, these membranes exhibit peculiar ion selectivity and diffusivity properties [15,16]. While this unique, tortuous nanoslit system shows some unusual ion or water transport properties [12,17–19], it remains difficult to quantitatively analyze, compare and substantiate its performance against the conventional membrane systems. Taking the multilayered graphene membranes as an example (Fig. 1a), the key microstructural parameters of the membrane include the interlayer distance, size and shape of single layer graphene sheets, pin-hole distribution, out-of-plane corrugation and the component of residual functional groups. These parameters may significantly vary with the different synthesis processes [20,21]. A simplified representative structural model is needed to describe the cascading nanoslit microstructure so that quantitative analysis can be performed for this emerging class of membrane materials.

We have recently developed a new technique – capillary compression – to continuously tune the interlayer distance in multilayered graphene-based membranes from 12 nm to 0.5 nm [22]. Through a combination of experimental and continuum simulations, we proposed a two-dimensional statistical representative microstructure model for the membrane. As shown in Fig. 1, this structural model consists of face-to-face aligned graphene sheets, forming an array of nanoslits interconnected by some nanopores arising from either the defects in each graphene layer or the edge-to-edge gaps between adjacent graphene layers [23]. Our model indicates the importance of defects in graphene layers in terms of ion and molecule transport. With this model, we successfully revealed the ion transport scaling relation in the whole sub-
10 nm region [23].

Despite the success of using this 2D representative microstructural model to establish the ion transport profile in the sub-10 nm range, it remains unclear if this model is compatible with the traditional simple 1D model. The latter is widely used in studying the nanoporous membranes and electrochemical energy storage devices such as filtration polymer membranes [24], carbon nanotube membranes [25], micro/nano-fluidic devices fabricated on silicon chips [26] and electrochemical supercapacitors electrode [27].

In this paper, we explore the feasibility of developing an equivalent 1D nanochannel model, including only two structural parameters – the effective diffusion length $L_{ef}$ and effective cross-section area $A_{ef}$, for the multilayered graphene-based membranes. A systematical study of the ion transport process through a simplified 2D cascading nanoslit model was performed using continuum simulations. Through employing the time-lag method [28,29], we successfully demonstrate that an equivalent 1D nanochannel model can be established to represent these membrane structures. This new model is also found to largely agree with our experimental results with the complex 3D cascading nanoslit structure.

2. Methodology

To simulate the ion transport in the cascading nanoslit system, continuum simulations [30] were carried out by using the COMSOL Multiphysics simulation package. Fig. 1b depicts our simulation model consisting of 20 layers of 2D material sheets. This two-dimensional statistical representative microstructure can be described by using three structural parameters: the lateral size ($L$), aperture size ($d$), and channel height ($h$). In this model, the periodicity condition should be applied in $y$ and $z$ direction. KCl electrolyte was selected in our study. In short, $K^+$ and $Cl^-$ have similar ion size and diffusion coefficients ($D_{K^+}=1.84 \times 10^{-5}$ cm$^2$/s, and $D_{Cl^-}=1.91 \times 10^{-5}$ cm$^2$/s at concentration of 1 mol/L [26]). They can be modelled as a neutral ion pair in diffusion simulations with a diffusivity coefficient of $D=1.85 \times 10^{-5}$ cm$^2$/s [31]. Owing to this feature, KCl has indeed been widely used as a model electrolyte in the field of nanofluidics. The relatively high concentration (1 M in feed reservoir) is often adopted in energy storage applications. It enhances the diffusion flux and minimizes the surface adsorption effects in our experiments [23]. The transport of neutral particle is governed by Fick’s second law [32] in the grey region of Fig. 1b:

$$\frac{\partial n}{\partial t} = D \nabla^2 n \tag{1}$$

where $n$ is the concentration of the neutral particle. A constant concentration constraint was imposed at the entrance on left ($n=0.5$ M) and exit on the right ($n=0$ M) that mimics the constant concentration gradient through the graphene membrane in experiment setup. At graphene surfaces, the impermeable interface condition $V_{in}=0$ was adopted. Due to the periodicity, at the top and bottom surface, we also set $V_{in}=0$. In this work, a wide range of lateral sizes $L=8$–1000 nm was studied to cover the possible microstructures in experiments. The range of $h$ is 0.5–12 nm, and $d$ is in the range of 1–20 nm.

To establish an equivalent 1D nanochannel model, the time-lag method shown in Fig. 2 was employed. This method is widely adopted to analyze the ion trans-membrane transport properties in the membrane society [33]. Starting with a clean membrane separating a feed reservoir ($n>0$ M) and a drain ($n=0$ M), the amount of ion transport through the membrane $Q$ increases with time. Fig. 2 shows a general trend of $Q$ versus time $t$. It starts with a transient state and is followed by a steady state with the constant trans-membrane flux (gradient of $S_n$). The intersection of asymptotic line with the horizontal line of $Q=0$ is the so-called lag-time $t_n$.
Now let us assume the membrane consisting of multiple parallel one-dimensional channels passing through the membrane as depicted in inset of Fig. 2. The length of each channel is \( L_{\text{eff}} \) and total cross-section area of these channels is \( A_{\text{eff}} \). Solving the classic model (Eq. (1)), we can get the following relationship [33]:

\[
L_{\text{eff}} = \sqrt{6D_{tL}} \\
A_{\text{eff}} = \frac{S_{\infty}}{\Delta n^*D}L_{\text{eff}}
\]

where is the diffusion coefficient of ions in bulk solution; \( t_L \) is the lag time of diffusion; \( S_{\infty} \) is the gradient of \( Q(t) \) in the steady state; \( \Delta n \) is the concentration difference across the membrane. Given that the \( t_L \) and \( S_{\infty} \) can be determined from the \( Q(t) \) curves calculated in our numerical simulation of the 2D nanoslit systems (or directly measured in experiments), using Eqs. (2 and 3), we can establish an equivalent 1D nano-channel model. Moreover, through nondimensionalization analysis of Eq. (1), we find the selection of the constant diffusion coefficient and concentration difference applied at entrance and exit of the membrane will not affect the \( L_{\text{eff}} \) and \( A_{\text{eff}} \) results.

3. Results & discussions

The effective diffusion length of molecules or ions is one of the most important structural parameters for a porous membrane because of its direct influence on transmembrane permeance. Fig. 3a shows the variation of \( L_{\text{eff}} \) over the lateral size \( L \) (from 8 to 1000 nm) at different channel heights \( h \) (from 0.5 to 12 nm) given \( d = 2 \) nm. Overall the \( L_{\text{eff}} \) reduces with \( L \). The dashed line represents the relation \( L_{\text{eff}} = (N-1)L/2 \), which represents the case where ions strictly follow the center line of the cascading nanoslits under a condition of \( L \) much larger than \( h \). Thus, at a relative large \( L \) (> 200 nm), the \( L_{\text{eff}} \) follows the dashed line, showing a linear relationship with \( L \). It indicates that the transport in the parallel nanoslits is the dominant process. For the cases of relative small \( L \) and large \( h \), the \( L_{\text{eff}} \) deviates from the dashed line. This could be
partly understood by the inset in Fig. 3a. With the increase of $h$, the diffusion path in the nanoslit change from along the parallel direction to the diagonal one. In addition, with the reduction of lateral size $L$, the influence of the aperture region will be amplified, leading to the increased $L_{\text{eff}}$ value.

The influence of aperture $d$ on $L_{\text{eff}}$ at different channel heights $h$ is shown in Fig. 3b. The length $L$ is set as 55 nm, which is close to the value determined from our experiments [23]. For $h > 2$ nm, reducing the aperture size $d$ would significantly increase $L_{\text{eff}}$, showing an highly nonlinear dependence. Given a large channel height $h$, the small aperture opening ($d \ll 2h$) is the bottleneck of mass transport process, which could lead to the significantly enhanced effective length (Fig. 3b). At a relatively small height ($h \ll 2$ nm), the $L_{\text{eff}}$ is nearly independent on $d$. Again, this indicates that ion diffusion is mainly determined by the nanoslit. Interestingly, we find that at very small channel height $h < 0.5$ nm, $L_{\text{eff}}$ decreases with $d$, which is opposite to other cases. This counterintuitive variation is attributed to the ‘double channel height’ of the aperture region. In this situation, the volume of aperture region is much larger than that of the nanoslit region and the lag-time or the effective length is proportional to the void of the membrane. Then, with the shrinkage of the dominant aperture region, both $t_{\text{eff}}$ and $L_{\text{eff}}$ would reduce with $d$.

Another key structural parameter is the effective cross-section area $A_{\text{eff}}$. Fig. 4a shows the variation of $A_{\text{eff}}$ with $h$ at different aperture size $d$. The length $L$ is fixed at 55 nm. As expected, $A_{\text{eff}}$ increases with the channel height $h$. But they generally do not follow the linear relation $A_{\text{eff}} \propto (2h - h_c)$ shown as the dashed line except for the cases of $h < 2$ nm. $h_c$ is the thickness of the atomic layer graphene sheet where $h_c = 0.335$ nm was taken. The accounting of factor 2 here represents the split double flow shown in inset of Fig. 2. The curves tends to deviate from the linear relation with $h$. This could be attributed to the restriction from the aperture region. A larger aperture size $d$ leads to a higher effective area, which is reasonable to understand.

Fig. 4b shows the dependence of $A_{\text{eff}}$ on $L$ at different channel height $h$. The aperture size is fixed at 2 nm. The size $L$ does not directly affect $A_{\text{eff}}$. Its influence should arise from the relative proportion of nanoslit region over the aperture region. For large $L \geq 300$ nm, the $A_{\text{eff}}$ results approach a constant value, determined by the channel height and graphene thickness ($A_{\text{eff}} \propto (2h - h_c)$). Because aperture plays a negligible role in this case. For relative small $L$ ($< 100$ nm), the influence of aperture region becomes more apparent. For channel size $h < d$, the decrease of $h$ leads to an enhanced $A_{\text{eff}}$ with the reduction of $L$. While, the opposite trend is observed for $h > d$.

To verify the 1D equivalent model, the $L_{\text{eff}}$ and $A_{\text{eff}}$ simulation results were compared with those determined by using the time-lag method in our membrane experiments. Note that $L = 55$ nm and $d = 2$ nm were adopted in our simulations, which was taken from our previous work [23]. The results are summarised in Fig. 5a and b. Since $A_{\text{eff}}$ scales with number of graphene layers $N$, Fig. 5a shows the normalised results $L_{\text{eff}}/N$. The effective area scales with the membrane area $A_m$. Thus inverse $A_{\text{eff}}/A_m$ results are summarised in Fig. 5b. The overall agreement is good. The notable discrepancy in Fig. 5b at small channel height ($h < 0.5$ nm) could be attributed to the surface corrugation of the experiment graphene flakes or the strong solution-wall interaction in the cascading nanoslits.

The structural parameters: $L$, $d$ and $h$ that we studied in this paper, cover the whole range of possible membrane microstructures assembled by 2D materials, such as graphene and graphene oxide in experiments. Therefore, the results presented in Figs. 3–5 can be directly used to determine the quantitative 1D nano-channel model to analyze experimental results. They also provide quantitative information for membrane design. Since $L_{\text{eff}}$ scales with $N$ and $A_{\text{eff}}$ scales with $A_m$, appropriate normalisation should be employed when using these data.

We note that a 2D disordered model has been used by Chen et al. [34] to study mass diffusion in flake-filled polymer membranes via the Finite Element Methods (FEM) where the nano-platelets of clay/silica act as the impermeable barrier as atomic-thickness graphene flakes in the multilayered membranes [34]. Goodyer [35] and Greco [36] extended the study into ordered/disordered 3D models to obtain the diffusion flux in steady state. Compared with FEM, the Monte Carlo method is an alternative way to study mass diffusion through the membrane [37,38]. Comparison between the two methods shows good agreement in 2D models [30]. However, most of these studies focused on calculating the Barrier Improvement Factors, namely the diffusion flux drops in steady state by incorporating the impermeable clay into polymer substrate. To the best of our knowledge, no previous theoretic models were devoted to $L_{\text{eff}}$ and $A_{\text{eff}}$ for equivalent 1D nanochannel model. Our equivalent 1D model provides a convenient basis to interpret transmembrane ion permeance experiment data to gain semi-quantitative information regarding the ion transport in nano-slits, which is important for fundamental studies of novel ion transport properties at nanoscale. From the application perspective, our model can aid the quantitative structure design of membranes assembled by two-dimensional layered materials for energy storage [39–41] and ion filtration applications.

Both our 2D and 1D structure models provide statistical yet simplified description of the complex 3D structure of graphene gel membranes. For example, the “lateral size” of graphene $L$ in our 2D model
represents the statistically averaged distances between pin-holes/defects in graphene flake. In the future, it is desirable to establish clear connection of these statistically structure parameters with the complex structures in real 3D membranes to reveal in-depth structure-property relationships. Furthermore, the relatively large deviation observed in Fig. 5b for small slit size h~ 0.5 nm suggests that the corrugation of graphene flakes [42] or the specific adsorption of graphene surface [43] should be taken into account for developing a better structural model.

4. Conclusions

In this work, we have developed an equivalent one-dimensional ion transport path model for the tortuous nanoslit systems embedded in the multilayered graphene membranes. We find that for large L and small channel size h where diffusion in the nanoslit dominates, the effective diffusion length $L_{\text{eff}}$ and $A_{\text{eff}}$ can be calculated by using the simple formula as $(N - 1)L/2$ and $2(h-h_0)$, respectively. Otherwise, they show complex dependence on all three structural parameters of the 2D statistical representative structural model. The quantitative relations obtained in this study could be generally used for membranes assembled by 2D materials. The equivalent 1D model should provide a platform to interpret and rationalize experiment results of ion or molecule transport in the cascading nanoslit systems. It may provide a simple yet quantitative model to design 2D materials-based membranes for various applications, such as energy storage electrode design, ion separation, water desalination or treatment.

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