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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 ($> \sim 100$ 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

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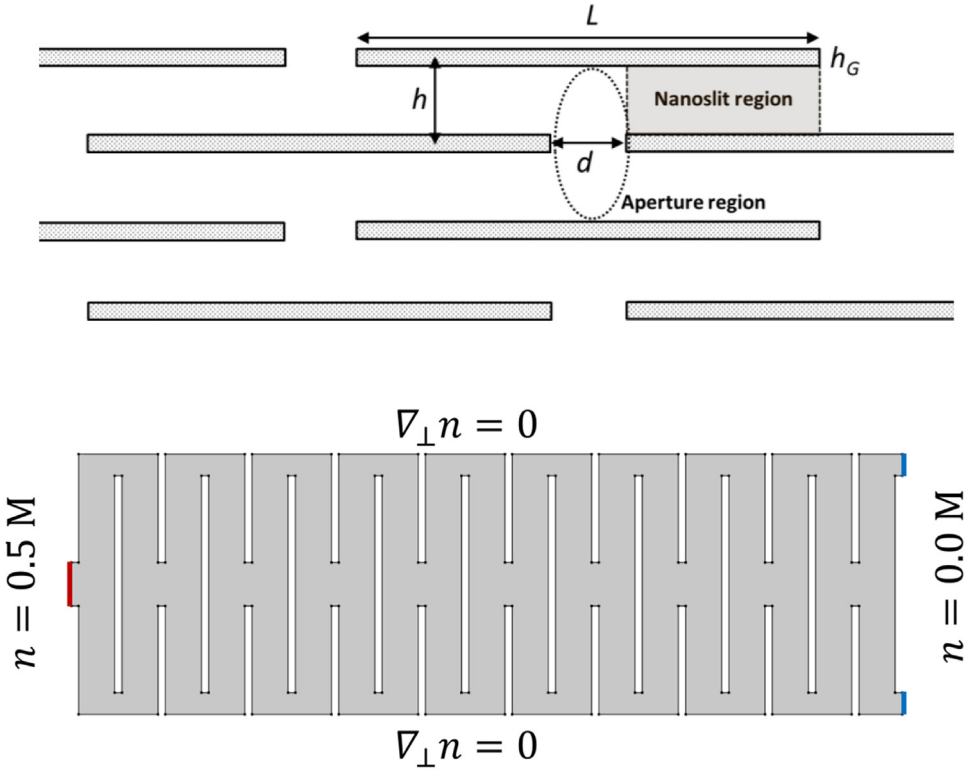

Fig. 1. a) Schematic diagram of recently proposed two-dimensional statistically representative microstructure model for the cascading nanoslit system embedded in multilayered membranes assembled by 2D materials. The long dashed horizontal sheets represent the impermeable 2D material flakes; L is the flake size; d is the aperture size or the edge distance between two adjacent sheets; h is the interlayer distance; and h_G is the thickness of individual graphene. b) A 2D continuum simulation model consists of 20 layers of 2D materials (e.g., graphene) with L= 10 nm, h= 2 nm and d = 2 nm; The left and right end is fixed with constant concentration for entrance (blue) and exit (red), respectively.

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_{eff} and effective cross-section area A_{eff}, 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 experiment 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+}= 1.84×10^{-5} cm^2/s, and D_{Cl+}= 1.91×10^{-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= 1.85×10^{-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= .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 $\nabla_\perp n = 0$ was adopted. Due to the periodicity, at the top and bottom surface, we also set $\nabla_\perp n = 0$. 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 nanochannnel 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