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Highly selective mixed-matrix membranes with layered fillers for molecular separation

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ABSTRACT

Two-dimensional (2D) layered porous materials are of a considerable interest to researchers due to differences in the sizes of in-plane and out-of-plane confinement. These layered materials have been blended with polymers for the fabrication of mixed-matrix membranes (MMMs) for applications involving separation. The polymers in MMMs serve as a matrix and the 2D layered materials serve as filler used to enhance the separation performance (diffusivity and selectivity) of the polymeric matrix. Unfortunately, the existing models for estimating the effective diffusivity of MMMs with layered fillers are unable to provide reliable predictions. This study proposed a numerical approach to the estimation of effective diffusivity and the selectivity of MMMs using layered fillers based on the mass transfer simulations. In the proposed models, we took into account two critical parameters of the layered fillers: anisotropic diffusivity and orientation distributions. The predictive ability of the proposed approach was evaluated via comparison with experimental data. Finally, we outline the design of highly selective MMMs with layered porous materials based on the proposed methodology.

1. Introduction

Layered microporous nanomaterials have attracted considerable interest from researchers due to their two-dimensional (2D) structure [1–4]. Layered zeolites and other layered clay materials have been widely applied in catalysis and the fabrication of nanocomposites [5–9]. Zeolitic imidazole frameworks (ZIFs) are an emerging class of microporous material, and a layered ZIF, ZIF-L has been recently reported [10–12]. Like other microporous materials, layered microporous nanomaterials can be used in molecular separation. One common means of applying these nanomaterials to the process of separation involves blending them with polymers to form composite membranes [13–20]. These nanocomposite membranes are commonly referred to as mixed-matrix membranes (MMMs) using polymeric materials as the matrix and nanoporous materials as the filler [2,21–30]. In the initial development of MMMs, only nearly spherical microporous materials were used as fillers [26,31]. In recent years, low-dimensional (1D and 2D) porous materials, such as nanotubes (1D) [32–35] and layered porous materials (2D) [36–38], have been regarded as emerging filler materials. Layered porous materials could potentially outperform near-spherical ones for use as filler in MMMs, for two reasons. First, the high aspect ratio of layered materials in the MMMs enables control over the orientation. Second, cross-plane and in-plane confinement in the layered porous materials usually differs in size, which leads to anisotropic diffusivity in the layered microporous materials. For example, MCM-22 [39,40] and AMH-3 [41,42] are known to have cross-plane pores smaller than in-plane confinement. The controllable orientation and anisotropic diffusivity caused by differences in the in-plane and cross-plane confinement of the layered porous materials are unique features capable of maximizing the effective diffusivity and selectivity of MMMs. MMMs with graphene-based fillers have recently been shown to have extraordinarily high permeability and selectivity [43–47].

Diffusivity and selectivity are the most critical factors in evaluating the performance of MMMs. The diffusive selectivity is defined as the ratio of diffusivity between two transported species. In the case of spherical fillers with isotropic diffusivity, effective diffusivity can be estimated analytically using the Maxwell model [27,48,49]:

$$D_{eff} = D_m\left[\frac{D_f + 2D_m - 2(D_m - D_f)\Phi_f}{D_f + 2D_m + (D_m - D_f)\Phi_f}\right] \quad (1)$$

where D_{eff} is the effective diffusivity, D_f and D_m are the intrinsic diffusivity of the filler and matrix, respectively, and Φ_f is the volume fraction of the filler material. Analytical models of MMMs

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with tubular [50] or layered [51–53] fillers have also been proposed. For example, the Cussler model takes into account the aspect ratio of the layered fillers:

$$D_{eff} = D_m\left[1 - \Phi_f + \left(\frac{1}{\frac{D_m}{D_f}} + \frac{1-\Phi_f}{\alpha^2 \Phi_f^{\,2}}\right)^{-1}\right]^{-1} \tag{2}$$

where α represents the aspect ratio; i.e., the ratio of the in-plane diameter and thickness of the fillers. However, derivation of analytic models usually involves assumptions, which tend to oversimplify the system and thereby reduce the accuracy of the predictions related to diffusivity. For example, significant disagreements have been observed between experiment measurements and the predictions of D_{eff} by the Cussler model when dealing with MMMs comprising cellulose acetate as a matrix and AMH-3 as a filler [54].

Numerical methods based on mass transport simulations have been developed to address this issue [55–61]. In the case of MMMs with layered fillers, numerical methods have been developed to investigate the effects of aspect ratio [58], filler shape (e.g., circular, square, hexagonal) [59], and filler orientation [55–57] on the D_{eff} of MMMs. Although these studies take into account details of the layered fillers related to morphology and orientation, the key feature of the layered porous materials (anisotropic diffusivity) is not included in the mass transport simulations. In other words, isotropic diffusivity is used to describe mass transfer in the fillers, which can lead to highly erroneous predictions related to the D_{eff} of MMMs comprising layered porous fillers. In fact, few of the aforementioned reports have opted to compare their predicted D_{eff} values with experiment-derived results, and what comparisons are available reveal considerable disagreement between the calculated and measured D_{eff} values [56].

In this study, we developed a simulation of the mass transfer of MMMs with layered fillers, which also takes into consideration anisotropy in the diffusivity of the filler. A second order tensor was used to describe anisotropy in the diffusivity of the layered fillers, as follows:

$$\overrightarrow{\overrightarrow{D}}_f = \begin{bmatrix} D_{f,xx} & D_{f,xy} & D_{f,xz} \\ D_{f,yx} & D_{f,yy} & D_{f,yz} \\ D_{f,zx} & D_{f,zy} & D_{f,zz} \end{bmatrix} \tag{3}$$

where $\overrightarrow{\overrightarrow{D}}_f$ is the tensor form of the filler diffusivity, in which the component $D_{f,ij}$ represents the ability of the filler to cause molar flux in the i-direction under a concentration gradient in the j-direction. For fillers with anisotropic diffusivity, Fick's law of diffusion can be written as follows:

$$\overrightarrow{J} = -\overrightarrow{\overrightarrow{D}}_f \cdot \overrightarrow{\nabla} C \tag{4}$$

where $\overrightarrow{J}$ is the flux vector of the transported species and $\overrightarrow{\nabla} C$ is the concentration gradient vector of the transported species. For fillers with isotropic diffusivity, the non-diagonal component of the diffusivity tensor is zero and all three diagonal terms are identical. In this case, the diffusivity tensor $\overrightarrow{\overrightarrow{D}}_f$ can be reduced to a scalar D_f, deduced from Fick's law of diffusion as follows:

$$\overrightarrow{J} = -\overrightarrow{\overrightarrow{D}}_f \cdot \overrightarrow{\nabla} C = -\begin{bmatrix} D_f & 0 & 0 \\ 0 & D_f & 0 \\ 0 & 0 & D_f \end{bmatrix} \cdot \overrightarrow{\nabla} C = -D_f \overrightarrow{\nabla} C \cdot \tag{5}$$

We also investigated how anisotropy in the diffusivity of the filler influenced the D_{eff} of MMMs with layered porous fillers. Our results were compared with predictions obtained using the Maxwell and Cussler models, as well as previously reported experiment data. More importantly, we outline the means by which to take advantage of anisotropy in the diffusivity of the layered porous fillers for the design of high-performance MMMs (i.e., MMMS with high effective diffusivity and high selectivity).

2. Computational methods

2.1. Construction of mixed-matrix membrane model

We developed an algorithm for the creation of models describing MMMs with layered fillers under various filler volume fractions (Fig. 1a). The location of each filler within the matrix was randomly assigned using the Monte Carlo method. The tilt angle between the tilted filler and direction of bulk mass transfer (z-direction) is denoted by φ (φ ranges from 0 to $\pi/2$), as shown in Fig. 1b. When an MMM model was first created, the φ of each filler was set to zero; i.e., the matrix and all fillers were oriented in the same direction. Another algorithm based upon the Monte Carlo method was used to randomly assign a non-zero value φ for every filler. Due to spatial restrictions, fillers in MMM models with low filler volume fraction generally possess higher φ values. The MMM models constructed using the abovementioned method were then used for the mass transfer simulations outlined in the following section.

2.2. Mass transfer simulations

Fick's law of diffusion (Eq. (4)) was used to describe mass transfer in the MMMs with layered porous fillers. The cross-plane vector of the MMM models was aligned with the z-axis, such that the bulk mass transfer of the MMMs was in the z-direction. The diffusivity of the matrix was assumed to be isotropic. In accordance with Eq. (5), only a single value was required to describe isotropic diffusivity in the matrix phase. Because fillers in this study were permitted anisotropic diffusivity, a second tensor Eq. (3) was also required to describe diffusivity. In the case of layered fillers with the out-of-plane vector aligned with the z-axis (i.e. $\varphi = 0$), the diffusivity tensor can be expressed as follows:

$$\overrightarrow{\overrightarrow{D}}_f = \begin{bmatrix} D_{f,in} & 0 & 0 \\ 0 & D_{f,in} & 0 \\ 0 & 0 & D_{f,out} \end{bmatrix} \tag{6}$$

where $D_{f,in}$ represents the in-plane diffusivity and $D_{f,out}$ represents out-of-plane diffusivity of the layered filler (Fig. 1c). In the case of layered fillers rotated along the x-axis with a rotation angle θ_x, diffusivity is represented as follows:

$$\overrightarrow{\overrightarrow{D}}_f = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta_x & -\sin\theta_x \\ 0 & \sin\theta_x & \cos\theta_x \end{bmatrix} \begin{bmatrix} D_{f,in} & 0 & 0 \\ 0 & D_{f,in} & 0 \\ 0 & 0 & D_{f,out} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta_x & \sin\theta_x \\ 0 & -\sin\theta_x & \cos\theta_x \end{bmatrix}. \tag{7}$$

In the case of layered fillers rotated along the y- or z-axis with a rotation angle θ_y or θ_z, deducing the diffusivity tensor after rotation is analogous to Eq. (7), in which the rotation matrix is used for y- or z-axis rotation, respectively (Fig. 1d).

2.3. Numerical methods and post-processing of solutions

This study employed finite element analysis (FEA) to solve Fick's diffusion equation in order to obtain concentration profiles for the MMM models. In this work, FEA was implemented using