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Predictions of effective diffusivity of mixed matrix membranes with tubular fillers

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ABSTRACT

We report a method for estimating the effective molecular diffusivity of mixed matrix membranes (MMMs) with tubular fillers. This method is based on constructing three-dimensional MMM models for solving Fick's diffusion equation to obtain the concentration profiles. The effective diffusivity of the MMMs was thus derived from the concentration distributions. Using this approach, the effects of various structural parameters, including the tubular filler volume fraction, spatial distribution, orientation, aspect ratios, and diffusivity ratios, were assessed. The results suggest that the tubular filler alignment and spatial distributions are critical to the mass transfer in MMMs. We compared the diffusivity estimated by the presented method to the experimental data. Our approach shows improved predictions compared with the Maxwell model and the Kang–Jones–Nair (KJN) model. Overall, this work presents a useful tool for understanding and designing MMMs with tubular fillers.

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1. Introduction

Over the past two decades, nanotubes have been used increasingly as materials for membrane separation applications because of their high molecular diffusivity [1–4] and unique one-dimensional (1D) geometry, which allows for alignment of nanotubes in the membranes [5–13]. Since the discovery of single-walled carbon nanotubes [14], many studies have reported that high-flux carbon nanotube membranes can be created by orderly aligning nanotubes in membranes along the out-of-plane direction [2–4,11–13]. Although the ability to mass transport carbon nanotube membranes is appealing, the mass production of carbon nanotubes remains challenging, thus limiting their applications to large-scale industrial processes. To address this problem, metal oxide nanotubes, such as aluminosilicate [15–17] and titanate [18,19] nanotubes, have been investigated. These inorganic nanotubes can be synthesized under hydrothermal or solvothermal conditions. Techniques for engineering their dimensions [20–23] and surface functionality [15,24–27] have also been developed. However, only a few examples have been reported on the separation applications of metal oxide nanotube-polymer composite membranes [16,19].

The nanoporous material-polymer composite membranes for separation procedures are typically referred to as mixed matrix membranes (MMMs). The zeolite-polymer MMMs have been well studied [28–34]. MMMs with zeolites as fillers have been applied to oxygen/nitrogen (i.e., air) separation [31], alcohol/water pervaporation [28], and carbon dioxide/methane separation [35]. On the other hand, metal-organic frameworks (MOFs) with controllable surface properties have emerged as a new class of filler materials for MMMs [36–45]. To evaluate the separation performance of MMMs, the effective diffusivity and selectivity, which is the effective diffusivity ratio between two transported species, are frequently regarded as the figures of merit. Several analytical models have been proposed for estimating the effective diffusivity of MMMs with spherical or near-spherical fillers (e.g., zeolites or MOFs) [46–48]. The Maxwell model [49–51] is a well-known analytical tool for this type of estimation:

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

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 filler volume fraction. A numerical technique that accounts for numerous structural details of MMMs with spherical fillers was also developed for enhancing the reliability of D_{eff} calculations [52].

Despite the development of tools for predicting the diffusivity of MMMs with spherical fillers, only a few analytical models are available for MMMs with tubular fillers [6,53], including the Kang–Jones–Nair (KJN) model [6]:

$$\frac{D_{eff}}{D_m} = \left[1 + \frac{\cos\theta}{\cos\theta + \frac{1}{\alpha} \cdot \sin\theta} \left(\frac{D_m}{D_f \cdot \cos^2\theta} - 1 \right) \Phi_f \right] \quad (2)$$

where α is the filler aspect ratio and θ is the filler orientation with respect to the out-of-plane direction of a membrane. The KJN model can account for the orientation and aspect ratio effects of

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tubular fillers, but a 1D mass transfer approximation is involved during its derivation. This approximation may not appropriately capture the three-dimensional (3D) mass transport phenomena that occur in heterogeneous membranes, and may cause uncertainty about the reliability of the KJN model. The lack of reliable tools for predicting D_{eff} may be one of the key factors that retard the development of MMMs with tubular fillers for separations. To address this problem, we report herein a new approach for estimating the D_{eff} of tubular filler-containing MMMs. This method is based on the construction of 3D MMM models for solving Fick's diffusion equation, from which D_{eff} can be deduced from the acquired concentration distributions. Using this approach, the effects of the filler spatial distribution, orientation, aspect ratio, and diffusivity ratio on D_{eff} were evaluated. During the investigations, we determined the critical structural properties that affected the mass transfer in MMMs. Finally, we assessed the accuracy of the proposed method for estimating the D_{eff} of MMMs with tubular fillers by comparing our predicted D_{eff} to the experimental data and the Maxwell model and the KJN model predictions.

2. Computational methods

2.1. Mixed matrix membrane model construction

For the mass transfer simulations for MMMs with unidirectionally oriented tubular fillers, a “cylinder-in-a-box” building block was constructed (Fig. 1a). The box and cylinders mimicked the matrix phase and filler phases, respectively. A homemade algorithm was used to create the model with the targeting filler volume fraction, spatial distribution, aspect ratio, and orientation.

2.2. Modeling mass transfer

Fick's diffusion equation was employed in both the matrix phase and the filler phase to model mass transfer in MMMs:

$$\vec{J} = -\vec{\vec{D}} \cdot \vec{\nabla} C \tag{3}$$

where $\vec{J}$ is the diffusive molar flux of the transported species, $\vec{\vec{D}}$ is the diffusivity tensor, and ∇C is the concentration gradient. The boundary conditions for the mass transfer simulations are illustrated in Fig. 1d. The anisotropic diffusion properties of the tubular fillers were demonstrated by applying the no-flux boundary conditions to the side walls of the cylinders in the model. The concentration continuity was applied at the nanotube pore mouth–matrix interfaces, assuming that both phases had identical solubility for the transported molecules. A fixed concentration of 1 mol/m^3 was specified at one of the surfaces of the box normal to the z-axis, serving as the feed side of the membrane. The opposite surface served as the permeate side of the membrane and had a fixed concentration of 0 mol/m^3. The four remaining sides, parallel to the z-axis, were assigned no-flux boundary conditions.

2.3. Numerical methods and solution postprocessing

The concentration distributions of the MMM models were obtained by numerically solving Fick's diffusion equation (Eq. (3)) by using the finite element method (FEM) (Fig. 1b and c). The FEM was implemented using COMSOL Multiphysics®. The maximum mesh element size for the FEM was 1 μm, whereas the minimum mesh element size was 10 nm. A stationary fully coupled linear direct solver was applied. The preordering algorithm, a nested

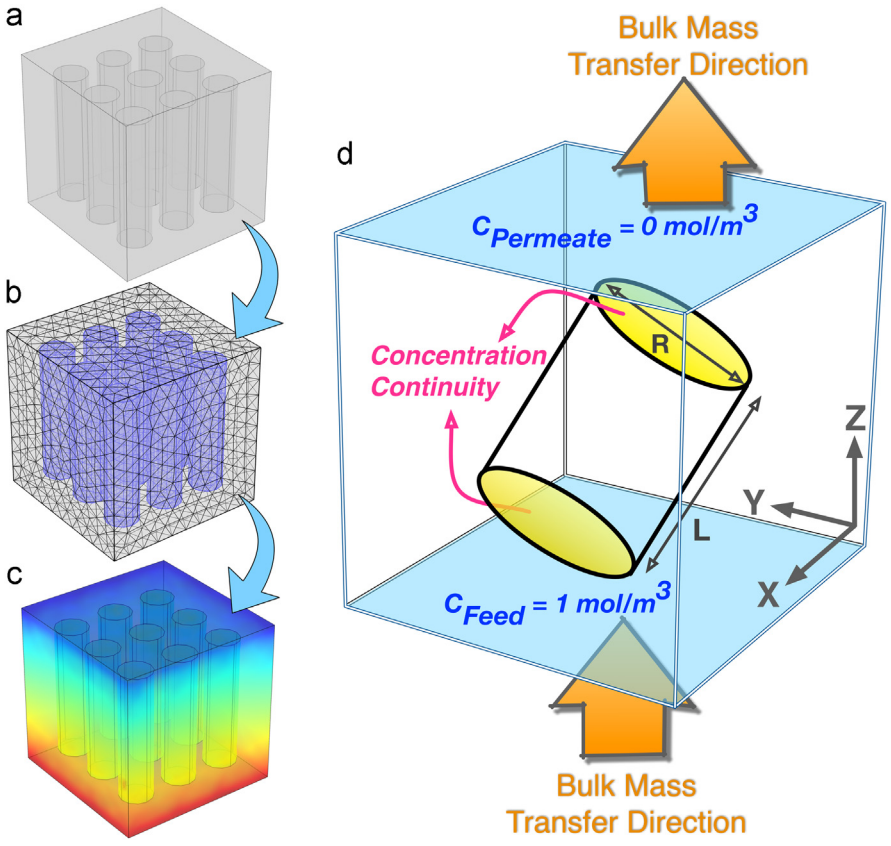

Fig. 1. Schematic illustration of the mass transfer simulations: (a) “cylinder-in-a-box” building block; (b) meshes for FEM; (c) concentration profile of the model; and (d) boundary conditions applied for the simulations. All the transparent surfaces in (d) represent no-flux boundary conditions.

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