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Estimation of the porosity of a chitosan–carbon nanoparticle membrane fabricated on a chip: A solute transport-based study

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ABSTRACT

Porosity is an important parameter by which to evaluate membrane performance. In recent years, membranes formed in microfluidic chips using laminar flow-based interfacial reaction technology have gained extensive attention due to their potential in micro-separation applications; however, so far, there has not been a feasible method to determine the porosity because of the very tiny size of this type of membrane. Here, we proposed a solute transport-based method to estimate the porosity of a chitosan–carbon nanoparticle membrane fabricated in a microdevice. In this method, a counter-current microdialysis mode was designed to experimentally study urea transport across the membrane, and a fluorescein was added to the urea solution to facilitate the observation of the urea concentration profile. Then, a porosity-related mass transfer model was developed to theoretically simulate the urea transport. The membrane porosity was obtained by iterating the porosity distribution to minimize the difference between the theoretical and experimental results. Finally, the membrane porosity was experimentally validated through a creatinine clearance study. The averaged porosities of the on-chip chitosan–carbon nanoparticle membrane formed in 15, 20, and 25 min were 0.356 ± 0.050, 0.242 ± 0.018 and 0.235 ± 0.009, respectively. The method proposed here is of significance for characterizing the performance of on-chip fabricated membranes.

1. Introduction

Membranes have been widely used in various areas, such as separation [1], extraction [2], dialysis [3], and filtration [4]. Over the past decade, with the rapid development of microfluidics technology, the fabrication of membranes on chips for various physical, chemical and biological applications has attracted a great deal of interest [5–8].

Today, there are three main approaches to fabricating a membrane on a chip. The first approach is to apply photopolymerization technology to form membranes in microdevices [8–10]. The second approach is based on a chemical etching technique [11–13]. The last approach is to use the laminar flow-based interfacial reaction technology for the *in situ* fabrication of membrane [14–16]. The commonality of membranes fabricated with these techniques is very tiny, making the separation and extraction of micro-samples possible. Compared to the integration approach in which the commercial membrane is directly sandwiched between two PDMS layers, the above approaches solve the problem of the sealing difficulty, but they produce a new difficulty. This new difficulty is due to the very tiny size of the membranes in microfluidic devices; it is hard to determine the characteristic parameters of membranes, such as porosity, permeability, and specific surface area.

Porosity is one of the intrinsic characteristics of membranes. It significantly affects the separation performance of membranes. Traditionally, the mercury intrusion-extrusion porosimetry method [17,18], the water evaporation method [19], the pycnometry method [20], and the thermoporosimetry and cryoporometry method [21] have been used to determine the porosity of membranes. However, these methods are not feasible for microfabricated membranes because the size of these membranes is very tiny.

Therefore we propose here a method to estimate the porosity of membranes fabricated on a chip. In our previous work, a chitosan–carbon nanoparticle composite membrane was fabricated in an

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Nomenclature

a	slope of the porosity distribution function
b	intercept of the porosity distribution function
c	concentration (mM)
D_e	solute effective diffusion coefficient (m^2/s)
D_0	solute free diffusion coefficient (m^2/s)
$\boldsymbol{I}$	unit tensor
k	permeability (m^2)
$\boldsymbol{n}$	unit normal vector
p	pressure (Pa)
Q_D	flow rate of DI water
Q_S	flow rate of urea/creatinine solution
$\boldsymbol{u}$	velocity vector (m/s)

Greek

ε	porosity ($0 \sim 1$)
μ	fluid viscosity ($N{\cdot}s/m^2$)
ρ	fluid density (kg/m^3)

Subscripts and superscripts

1,2,3	1, solution zone; 2, water zone; 3, membrane zone
T	transpose of a matrix

H-shape microfluidic device using laminar flow-based interfacial reaction technology. In this paper, we estimate the porosity of the composite membrane using the proposed method. First, a designed microdialysis experiment was performed in which a solution containing urea was introduced on one side of the fabricated membrane and deionized water was pumped through the other side counter-currently. Then, a porosity-related mass transfer model was used to theoretically simulate the urea transport across the membrane. The porosity was obtained by fitting the theoretical results to the experimental ones. Finally, to validate the accuracy of the porosity fitted, a creatinine clearance experiment was performed. The contribution of this work is as follows: (1) a solute transport-based method is proposed to estimate the porosity of a very tiny membrane fabricated in a microdevice; (2) the counter-current microdialysis mode is adopted to enhance the solute transport across a very tiny membrane so that the change in the solute concentration is detectable in practice; (3) a fluorescein is used to facilitate the observation of the solute concentration profile; and (4) the porosity of the on-chip chitosan–carbon nanoparticle composite membrane in our previous work is estimated.

2. Theory

In this paper, a solute transport-based method is proposed to study the porosity of a chitosan–carbon nanoparticle membrane fabricated on a microchip based on the fact that both the ultrafiltration and the solute transport across the tiny membrane are related to the porosity. In the method, a solution containing a certain solute flows on one side of the membrane, whereas deionized water counter-currently flows on the other side (Fig. 1). Based on a set of porosity-related flow velocity and solute concentration equations, the porosity can be obtained by fitting the theoretical results to the experimental ones.

To develop a mass transfer model to describe the solute transport, the following assumptions were adopted: (1) the fluid in all zones is Newtonian; (2) the diffusivity in the microchannels is uniform; (3) the carbon nanoparticles are homogeneously dispersed in the composite membrane; (4) the mass transport of the diluted solute does not affect the flow velocity field; (5) the size of the formed nucleus is uniform; and (6) the solution properties (i.e., density and viscosity) are the same as the water properties at room temperature.

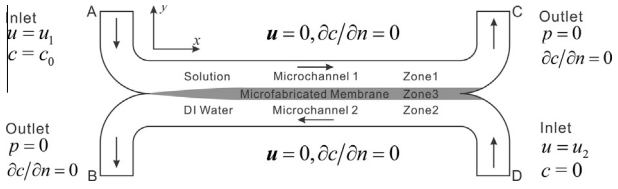

Fig. 1. Schematic diagram of the counter-current microdialysis process.

2.1. Velocity equations

In the two microchannels shown in Fig. 1, the solution and water velocity fields can be obtained using the Navier–Stokes equations. The flow in the porous membrane is described by the equation in [22–25]. The velocity equations for the three zones are listed as follows:

$$\text{Zone 1}: \rho\nabla\cdot\boldsymbol{u}_1 = 0 \tag{1}$$

$$\rho(\boldsymbol{u}_1\cdot\nabla)\boldsymbol{u}_1 = \nabla\cdot[-p\boldsymbol{I} + \mu(\nabla\boldsymbol{u}_1 + (\nabla\boldsymbol{u}_1)^T)] \tag{2}$$

$$\text{Zone 2}: \rho\nabla\cdot\boldsymbol{u}_2 = 0 \tag{3}$$

$$\rho(\boldsymbol{u}_2\cdot\nabla)\boldsymbol{u}_2 = \nabla\cdot[-p\boldsymbol{I} + \mu(\nabla\boldsymbol{u}_2 + (\nabla\boldsymbol{u}_2)^T)] \tag{4}$$

$$\text{Zone 3}: \rho\nabla\cdot\boldsymbol{u}_3 = 0 \tag{5}$$

$$0 = \nabla\cdot[-p\boldsymbol{I} + (\mu/\varepsilon)(\nabla\boldsymbol{u}_3 + (\nabla\boldsymbol{u}_3)^T)] - (\mu/k)\boldsymbol{u}_3 \tag{6}$$

where the subscripts 1, 2, and 3 denote Zone 1 (solution), Zone 2 (water) and Zone 3 (membrane), respectively; ρ is the density of the fluid; $\boldsymbol{u}$ is the velocity vector of the fluid; p is the pressure; μ is the dynamic viscosity of the fluid; $\boldsymbol{I}$ is the unit tensor; ε is the localized porosity of the porous membrane; and k is the permeability of the porous membrane (which can be calculated by $k = 4\varepsilon^3 r^2/[150(1-\varepsilon)^2]$ according to the literature [26], where r is the equivalent chitosan cluster radius).

2.2. Concentration equations

The solute transport from Zone 1 to Zone 3 is dominated by convection and diffusion. The concentration equations in the three zones are written as follows:

$$\text{Zone 1}: \nabla\cdot(-D_0\nabla c_1) + \boldsymbol{u}_1\cdot\nabla c_1 = 0 \tag{7}$$

$$\text{Zone 2}: \nabla\cdot(-D_0\nabla c_2) + \boldsymbol{u}_2\cdot\nabla c_2 = 0 \tag{8}$$

$$\text{Zone 3}: \nabla\cdot(-D_e\nabla c_3) + \boldsymbol{u}_3\cdot\nabla c_3 = 0 \tag{9}$$

where c is the solute concentration, D_0 is the solute free diffusion coefficient, and D_e is the solute effective diffusion coefficient in the porous membrane (which can be calculated by $D_e = D_0[\varepsilon^2/(2-\varepsilon)^2]$ according to the literature [27]).