Fabrication and Characterization of Single Pores for Modeling Mass Transport across Porous Membranes

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Received July 13, 1998. In Final Form: December 2, 1998

An Au membrane containing a single pore was fabricated using a template approach. The pore diameter is defined by the diameter of a glass fiber template and the pore length by the amount of Au electroplated over a seed pore. The utility of the single pore for modeling mass transport is demonstrated by configuring the pore as a Coulter counter to monitor the transport of 440 nm diameter polystyrene spheres. An important advantage of this Au membrane model is that the pore surface chemistry can be modified with a self-assembled monolayer. However, the metallic Au surface also requires minimizing the exposed membrane area in order to reduce the interfering charging/faradaic current and to shorten the instrumental response time.

Introduction

Mass transport, particularly molecular transport, in nanoporous media is of interest to chemists for many technologically important reasons: including zeolite-based catalysis, separation using various forms of chromatography, chemical detection in porous matrices, and cellular activity of membrane proteins.1-4 To gain a fundamental understanding of mass transport kinetics, we are beginning to build membrane models that contain only a single nanopore. Initially, we wish to examine the effects of three structural parameters on the rate of transport: namely, the diameter, the length, and the surface chemistry of the pore (Scheme 1).

Two major types of model membranes have been used in previous studies. The first type contains an array of pores with polydispersed pore diameter, pore length, and surface sites.5-7 Quantitative analysis of the data obtained from such a model is complicated although qualitative insights about transport mechanisms can be obtained.8-10 The second type of model membrane contains pores with one or more monodispersed structural parameters.11-17

Scheme 1

This model permits a more direct and quantitative correlation between the membrane structure and the transport rate because all pores behave identically. However, under steady state conditions, only an averaged transport rate can be determined because particles being transported do not enter membrane pores at the same time so that the measured signal is a spatially and temporally averaged one. In addition, it is increasingly difficult to ensure structural uniformity as the pore dimensions decrease. Sometimes only one structural parameter can be kept uniform. For example, the pore diameter of a track-etched polycarbonate membrane is uniform but the pore length varies slightly because of the dispersion in the track tilt angle.18

In contrast, the single-pore model presented here allows examination of individual stochastic transport.

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Figure 1. Schematic illustration of a template method for fabricating single pore membranes: (A) insertion of a glass template fiber into a seed pore across a free-standing Au membrane, (B) controlled deposition of an Au layer via electroplating, resulting in simultaneous diameter reduction and length elongation of the seed pore; (C) chemical removal of the template fiber with concentrated HF (48%).

Results and Discussion

Figure 2 shows optical micrographs of a single pore fabricated according to the above template method. Although measuring the pore diameter is straightforward, the inner pore surface cannot be imaged easily. One might speculate that the pore surface is as rough as the surface beyond the rim of the pore (Figure 2A), however, we think that the roughness is defined primarily by the fiber surface. Since a very slow electroplating rate is used, the film growth is far from the diffusion-controlled regime. It


(21) Microtechnology Laboratory (MTL), University of Minnesota.


(23) Electrochemical etching or plating were controlled with a PINE potentiostat (model AFRDES, PINE Instrument, Grove City, PA).

(24) At this point, the Au surface may be modified with a SAM; however, this work only involves bare Au surface which is covered later by specifically adsorbed Cl ions.

(25) The RMS (root-mean-square) roughness obtained from a STM image of the membrane surface is about 93 nm.
is unlikely that any void space is trapped between the fiber surface and the pore surface. The fiber template is an important feature of our method for pore fabrication. Using the fiber ensures effective control over both pore diameter and pore length. From Figure 1, one can see that the pore diameter is equal to the fiber diameter while the pore length is about twice the thickness of the electroplated Au (plus the seed membrane thickness). One problem of the present method is that it requires too many fabrication steps, which leads to a long fabrication time and a low device yield.

There exists a close correlation between the structural parameters of a nanopore (pore diameter, length, and surface chemistry) and its performance characteristics as a Coulter counter. The observed membrane current, $i_m$, across a single metallic pore can be written as

$$i_m = i_c + i_f + i_p$$  \hspace{1cm} (1)

where $i_c$ is the capacitive charging current and $i_f$ is the faradaic current across the membrane/electrolyte interface. $i_c$ is observable only when the membrane potential, $E_m$, changes. Charge neutrality requires that $i_f$ corresponds to a cathodic reaction at one side of the membrane while an equal magnitude of anodic current passes through the other side of the membrane. The ionic current across the pore itself, $i_p$, is given by eq 2

$$i_p = \frac{E_m}{R_p} = \frac{\kappa \tau_0^2 E_m}{4l}$$  \hspace{1cm} (2)

where $R_p$ is the pore resistance, $\kappa$ is the electrolyte conductivity, $d$ is the effective pore diameter, and $l$ is the pore length. $i_p$ will change when $R_p$ changes, e.g., when a particle moves into the pore, causing a decrease in the effective pore diameter $d$. Equation 2 ignores the "end effect," which introduces a significant error when the $l/d$ ratio approaches 1.\(^{27}\) The end effect originates from the ion flux extending outside the pore entrance or exit.

It is desirable to minimize $i_c$ and $i_f$: i.e., the capacitive and faradaic (CF) current since only a change in $i_p$ carries analytical information in a Coulter counter. Figure 3 shows the relative magnitude of the three current components. Without a pore, only the CF current is visible (Figure 3A); the rectangular loop is characteristic of a capacitor while the slight tilt is caused either by the electrolysis of trace redox impurities or by an unknown leakage pathway across the metal membrane.\(^{28}\) To reduce the CF current, the area of the exposed Au surface near the pore is


\(^{(28)}\) The leakage pathway, for example, may be located along the grain boundaries of a polycrystalline Au film.
The single pore reported here can be used as a Coulter counter to detect 440 nm diameter spherical particles. Single-pore Au membranes offer a convenient route for tailoring the surface chemistry of the pore with a SAM. However, Au membranes also show a drawback: the bare metal surface exposed to the electrolyte has to be minimized in order to decrease the interfering charging and faradaic current and to shorten the instrumental response time.

**Summary and Conclusion**

We have developed a template method for fabricating single-pore membranes. The method allows convenient control over the pore diameter and the pore length. We have also demonstrated that the single-pore membrane can be used as a Coulter counter to detect 440 nm diameter spherical particles. Single-pore Au membranes offer a convenient route for tailoring the surface chemistry of the pore with a SAM. However, Au membranes also show a drawback: the bare metal surface exposed to the electrolyte has to be minimized in order to decrease the interfering charging and faradaic current and to shorten the instrumental response time.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (CHE-9796203). Helpful discussions with Dr. Stephen W. Feldberg (Brookhaven National Laboratory) and Dr. Mark Spak (Hoechst Celanese) as well as technical assistance from Kevin Roberts (MTL) are greatly appreciated.

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(31) Do not confuse the uncompensated resistance (connected in series with the membrane capacitor) with the pore resistance (connected in parallel to the membrane capacitor).

(32) The equation, $t = \pi D c / k$, can be used to estimate the diffusional transient time, where $t$ is the pore length ($6.5 \mu m$) and $D (1 \times 10^{-6} cm^2/s)$ is the diffusion coefficient estimated from the Stokes–Einstein equation.

