

# Preparation and characterization of non-ionic block co-polymer templated mesoporous silica membranes

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## Abstract

We report on the preparation and characterization of mesoporous silica membranes via micellar templating using the non-ionic ethylene oxide–propylene oxide–ethylene oxide tri-block copolymer surfactant, Pluronic P123, as a template under various template/silica volume percentages ( $V_{TS\%}$ ). The silica membranes were prepared by dip coating silica sols onto porous  $\alpha$ -alumina supports followed by calcination to remove the template. The membranes were characterized by single gas permeation and permporometry measurements. Using a  $V_{TS\%}$  of 33 we found that silica membranes comprised of three dip/fire cycles resulted in highly reproducible continuous membranes with minimal defects. Helium and nitrogen permeance values were of the order of  $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . The pore size distribution, determined from permporometry measurements, indicated a dominant peak at 5 nm diameter and approximately 10% microporosity. In addition, there was 8–10% permeance through pores with diameters between 15 and 40 nm. At higher  $V_{TS\%}$  (47.5 and 65) the silica membranes had considerable bypass flow. The pore size distribution (PSD) of the membrane via permporometry indicated a shift to smaller values for the membrane when compared to the PSD of the powder from the calcined dipping sol, determined by nitrogen adsorption/desorption.

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## 1. Introduction

Mesoporous silica membranes and materials are receiving attention due to potential applications for ultrafiltration [1,2], matrices for organic modification [3,4], biological separations and drug delivery [5–7], idealized supports for pore size reduction, [8,9] and supports for microporous layers [10]. Since the discovery of surfactant templated silica [11] recent efforts in silica membranes have shifted from controlling pore size through interparticle spacing (resulting from the sintering of particulate sols) to controlling pore size through the size of the interconnected micelle structures (formed from surfactant aggregates) that template the silica framework. There are several advantages to preparing mesoporous silica membranes using micellar templating. For example, there is a potential to prepare membranes with a narrow pore size distribution, similar to what has

been achieved in powder formation for which pore size control within the 2–10 nm size range has been demonstrated [11,12]. Additionally, under specific synthesis conditions, the surfactant assemblies can arrange themselves crystallographically, yielding the potential to control pore orientation [13].

In general, the research trend has been to use synthetic strategies for powders and apply these to thin film synthesis. Typically, a dilute solution containing surfactant, a molecular source of silica (for example tetraethylorthosilicate, TEOS) and solvent is prepared at low pH to quench polymerization of the silica source. Thin film synthesis is then typically achieved via dip or spin-coating, although other routes are possible. Brinker and co-workers established an evaporation induced self-assembly (EISA) technique for preparing mesoporous thin silica films using surfactant assemblies where rapid evaporation of the dilute dipping solution induced the self-assembly of surfactant structures which templated the silica formation [14–16]. A good deal of work has been done on thin films formed on planar supports such as single crystal silicon or glass slides [12,13,17,18]. In addition to the work done on planar supports, there has been

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some work on porous supports, required for membrane fabrication as reviewed by Gulians et al. [13]. Typically, recipes for film formation on planar supports are used for porous supports. Important characteristics for membrane films on porous supports include pore size control, pore connectivity, porosity and the control of thickness and defects. If defects and pore size can be controlled then crystallographic arrangement of pores may be important in the overall permeance characteristics of the membrane.

Examples of mesoporous silica membranes prepared from surfactant templates include those made from both ionic surfactants [19,20] and non-ionic block copolymers [1,21]. These studies have demonstrated the successful formation of mesoporous silica membranes using micellar templating methods. Brinker et al. [22] demonstrated that silica membranes prepared using polystyrene-block-poly(ethylene oxide)(PS-*b*-PEO) as a templating agent resulted primarily in membranes with larger mesopores interconnected with micropores. Boissière et al. [1] prepared silica membranes using a nonionic polyethylene oxide (PEO)-based surfactant resulting in mesopores of 2.5 nm based on cut-off permeation experiments with PEO polymer solutions. A catalyst was used to localize the silica condensation reaction within the pores of the macroporous support.

In our work, we have prepared mesoporous silica membranes using an EO-PO-EO tri-block copolymer surfactant as a template under various template/silica volume fractions ( $V_{TS} = V_{\text{template}} / (V_{\text{template}} + V_{\text{SiO}_2})$ ) corresponding to cubic, hexagonal and lamellar organized structures, based on the work of Stucky et al. [12]. The silica membranes were prepared by dip-coating silica solutions onto porous  $\alpha$ -alumina disks. We have characterized these membranes using single gas permeation and permoporometry measurements. Here, we report: (i) the conditions for reproducible synthesis of low defect mesoporous silica membranes; (ii) the relationship between defect flow and  $V_{TS}$ ; and (iii) the comparison of the pore size distribution (PSD) of mesoporous silica membranes and the corresponding powders prepared from the membrane dipping solution. An increase in  $V_{TS}$  resulted in an increase in defect flow. In comparing the PSD's of the silica membrane and the silica powder prepared from the corresponding dipping sol, the PSD was shifted to smaller pore diameters for the membrane.

## 2. Experimental

### 2.1. Membrane preparation

Silica membranes have been synthesized using a tetraethylorthosilicate (TEOS) silica sol templated with Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, MW = 5800, BASF), a non-ionic block copolymer. Silica membranes were prepared with  $V_{TS\%}$  of 33, 47.5 and 65. For a typical synthesis of a thin mesoporous silica film a mixture of 5.4 mL H<sub>2</sub>O, 5.4 mL diluted HCl (pH 2.0), 15.2 mL EtOH, 11.1 mL TEOS (molar ratio of 1 TEOS:5.2 EtOH:12 H<sub>2</sub>O:0.015 HCl:0.021 P123) was stirred vigorously for 20 min. Then a mixture of P123 and EtOH was added to the solution and mixed until the P123 was dissolved, solutions were allowed to age at room temperature for 10 min (33  $V_{TS\%}$ )

to 3 h (47.5 and 65  $V_{TS\%}$ ) in a sealed container to prevent evaporation of EtOH. An asymmetric alpha alumina support disk with a 10  $\mu\text{m}$  top layer of 100 nm pore size (HiTK, Germany) was dipped into the solution, using a dipping apparatus, at a rate of approximately 2 cm/s. After dip-coating the macroporous support, the surfactant was then removed by sintering at a temperature of 400 °C for 4 h with a heating/cooling rate of 1 °C/min. This temperature was found to be sufficient to completely vaporize the surfactant in bulk experiments. The dip/fire procedure was repeated at least three times in order to ensure complete coverage of the support.

### 2.2. Porosity characterization

The mesoporous silica membranes were characterized using scanning electron microscopy (SEM), single gas permeation and permoporometry. Single gas permeation measurement with helium, nitrogen and methane were conducted between 25 and 150 °C at pressure drops between  $4.67 \times 10^4$  and  $1.13 \times 10^5$  Pa (350 and 850 Torr). SEM was performed with an AMRAY model 1810 scanning electron microscope. Mesoporous silica powders prepared from calcining the dipping solution were characterized using nitrogen porosimetry (ASAP 2010, Micromeritics).

The permoporometry measurement apparatus, shown in Fig. 1 was constructed based on reference [23]. The apparatus was constructed with 1/4 in. stainless steel tubing and fittings. Grade 5 helium was purified (Alltech He purifier) for water, oxygen and particulates and passed through two mass flow controllers (MKS Instruments). Mass flow controller 1 (MFC1, 0–50 sccm) fed the He stream into a stainless steel bubbler containing 99% *n*-hexane. The bubbler was allowed to reach equilibrium using the bypass valve at the bubbler outlet. Mass flow controller 2 (MFC2, 0–500 sccm) fed pure He to the membrane. The combination of flow through MFC1 and MFC2 allowed for the adjustment of hexane activity (hexane vapor pressure normalized to saturation pressure of hexane at experimental conditions) over a wide range. A pressure controller (0– $1.13 \times 10^5$  Pa; 0–1000 Torr), MKS Instruments was used to provide a constant feed pressure to the membrane.

The hexane bubbler temperature was maintained at 23 °C while the membrane cell temperature was maintained at 25 °C. The membrane was sealed in the testing cell with o-rings, tested for leaks, and heated overnight in flowing He at 110 °C prior to measurement. Typically pressures were maintained at  $3.87 \times 10^3$  Pa (29 Torr) above atmosphere. Flow rates of He through the membrane were measured using a soap bubble meter.

The activity of hexane was related to the pore size using the Kelvin equation

$$R_p = \frac{-4\sigma V_m}{RT \ln(a)} + t$$

where  $\sigma$  is the surface tension of hexane,  $V_m$  is the molar volume of hexane,  $R$  is the gas constant,  $T$  is temperature,  $a$  is hexane activity and  $t$  is the thickness of the adsorbed monolayer [24]. As the hexane vapor pressure is exposed to the membrane capillary condensation occurs in larger pores governed by the Kelvin

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