

Rapid communication

# Anodic alumina supported dual-layer microporous silica membranes

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## Abstract

We present a new processing scheme for the deposition of microporous, sol–gel derived silica membranes on inexpensive, commercially available anodic alumina (Anodisk™) supports. In a first step, a surfactant-templated mesoporous silica sublayer (pore size 2–6 nm) is deposited on the Anodisk support by dip-coating, in order to provide a smooth transition from the pore size of the support (20 or 100 nm) to that of the membrane (3–4 Å). Subsequently, the microporous gas separation membrane layer is deposited by spin-coating, resulting in a defect-free dual-layer micro-/mesoporous silica membrane exhibiting high permeance and high selectivity for size selective gas separations. For example, in the case of CO<sub>2</sub>:N<sub>2</sub> separation, the CO<sub>2</sub> permeance reached 3.0 MPU (1 MPU = 10<sup>-7</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>) coupled with a CO<sub>2</sub>:N<sub>2</sub> separation factor in excess of 80 at 25 °C. This processing scheme can be utilized for laboratory-scale development of other types of microporous or dense inorganic membranes, taking advantage of the availability, low cost and low permeation resistance of anodic alumina (or other metal oxide) meso- and macroporous supports.

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## 1. Introduction

Microporous inorganic membranes offer great potential for industrial gas, vapor and liquid separations on account of their good thermal, mechanical and chemical stability [1]. In addition, most microporous inorganic membranes offer higher permeance and higher selectivity than polymeric membranes, as a result of the presence of micropores that enhance transmembrane transport, and the pore wall rigidity that enhances selectivity. On the other hand, one of the most significant challenges in laboratory-

scale development as well as in commercialization of inorganic membranes is the difficulty in depositing these membranes in suitable porous inorganic supports with minimal defects [2]. Existing supports are either asymmetric ceramic (e.g. alumina) disks or tubes that can be made with fine top-layers (e.g.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) with pore size as low as 5 nm [3], or symmetric sintered metallic (e.g. stainless steel) disks or tubes that have much larger (>1  $\mu$ m) pore size [4]. Porous ceramic supports are usually more expensive and present issues with respect to sealing into high-temperature modules, whereas coarse-pore metallic supports require additional surface treatments or multiple repetitions of membrane deposition to ensure a continuous membrane layer [5].

Mesoporous silica layers derived from surfactant-assisted self-assembly processes have been proposed as suitable sub-layers in order to reduce the surface pore size of commercially available coarse-pore ceramic [6–10] or metallic [11] supports. Recent work demonstrated the possibility of depositing such layers on coarse-pore disk supports using hydrothermal reaction

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[7,8], dip-coating [8,9] or aerosol spraying [10,11] of surfactant/silica sols, however it remains a challenge to deposit such layers on tubular supports using practical deposition techniques such as dip-coating.

In this work, we demonstrate a simple processing scheme based on evaporation-induced self-assembly (EISA) of surfactant-templated silica sols [12] in order to utilize commercially available, inexpensive and high-flux porous anodic alumina disks as supports for depositing high-quality microporous inorganic silica membranes suitable for gas [6,13], vapor [14] or liquid separations [15]. Using EISA, the surface pores of the anodic alumina support are first filled with a mesoporous silica sublayer, thus reducing its surface pore size and facilitating deposition of a microporous gas separation membrane using spin-coating. This processing scheme can be extended to tubular supports as well as to other anodized metal oxide materials with higher chemical and/or thermal stability compared to  $\text{Al}_2\text{O}_3$  (e.g.  $\text{TiO}_2$  or  $\text{ZrO}_2$ ). Although our ultimate objective is to develop microporous and mesoporous silica-based membranes on such inexpensive supports for water desalination and purification, the success of the approach is demonstrated at this stage by depositing and testing a gas separation silica membrane prepared according to well-known polymeric silica sol–gel routes [13,16,17].

## 2. Experimental

### 2.1. Support

The support used for membrane deposition is commercially available Anodisk 25 (Whatman, UK) with bulk pore size of 200 nm and top-layer pore size of 100 or 20 nm (VWR cat. no. 28138-065 and 28138-067, respectively). The support has a diameter of  $\sim 25$  mm and is supplied with a polypropylene ring attached on its perimeter to allow for handling or sealing in membrane holders.

### 2.2. Silica sol preparation

Two types of surfactants were employed for preparation of the mesoporous sublayer to fill the pores of the Anodisk support. For the case of the 20-nm Anodisk, we employed Brij<sup>®</sup> 56 (Aldrich, MW = 683), while for the 100-nm Anodisk the choice was Pluronic<sup>®</sup> F127 (BASF, MW = 12,600). The different surfactant was selected so that the pore size of the sublayer is a reasonable average between that of the support and the membrane (roughly their geometric average). The Brij56 templated

silica sol was prepared by a two-step procedure as described elsewhere [6], while the F127-templated silica sol was prepared by a one-step procedure. Details of the preparation of the polymeric silica sols for deposition of the gas separation membrane layer are given elsewhere [13,16]. Table 1 shows the molar compositions of the different sols employed for the preparation of the mesoporous sublayer and gas-separation membrane.

### 2.3. Membrane deposition

Deposition of the mesoporous sublayer was carried out by suspending the Anodisk from its supporting ring with the aid of a self-closing tweezer, dipping it in the respective surfactant/silica sol (A or B, Table 1) for 5 s, and withdrawing it at a vertical speed of  $76 \text{ mm min}^{-1}$  with the aid of a precision linear translation stage (Compumotor, Series 850). The coated Anodisk was air-dried for 5 min and then calcined for 3 h at  $500^\circ\text{C}$  in an air oven to decompose the surfactant. Deposition of the microporous gas separation membrane layer was carried out by pouring 1 ml of the respective silica sol (C or D, Table 1) on the surface of the support until complete surface coverage, followed by spinning for 30 s at a speed of 2000 rpm with the aid of a commercial spin-coater (Headway Research, Inc.). The spin-coating process was carried out twice for each membrane. Calcination of the membrane was carried out for 3 h at  $300^\circ\text{C}$  under vacuum. All heating and cooling steps employed were carried out at a rate of  $1^\circ\text{C min}^{-1}$ .

### 2.4. Gas permeation

Gas permeation studies of Anodisk-supported membranes were performed using two custom-made stainless steel holders. A 2-port holder was employed to measure the compactness of as-deposited sublayers by transient vacuum permeation, while a 4-port holder was employed to measure binary permeation properties of the final membranes using a He sweep and a gas chromatograph (HP 5890 Series II) equipped with TCD for permeate composition analysis. In both cases the Anodisk support was placed on top of a  $10\text{-}\mu\text{m}$  pore sintered stainless steel support disk and sealed with the aid of silicon O-rings (Parker). All permeation testing was carried out at ambient conditions of temperature and pressure.

### 2.5. Characterization

Microscopical observations of the surface of the uncoated and coated Anodisk supports were performed with a Hitachi

Table 1  
Molar compositions of silica sols used for deposition of mesoporous sublayer (A and B) and microporous gas separation membrane layer (C and D)

Sol	Molar composition	Reaction condition	Ref.
A	1 Si–44 EtOH–5 H <sub>2</sub> O–0.004 HCl–0.08 Brij56	15 min agitation	[6]
B	1 Si–22 EtOH–5 H <sub>2</sub> O–0.007 HCl–0.007 F127	10–12 h stagnant aging at $25^\circ\text{C}$	–
C <sup>a</sup>	1 Si–3.8 EtOH–6.4 H <sub>2</sub> O–0.085 HNO <sub>3</sub>	3 h stirring with reflux at $60^\circ\text{C}$	[16]
D	1 Si–22 EtOH–5 H <sub>2</sub> O–0.4 HCl–0.2 NH <sub>2</sub>	24 h stagnant aging at $25^\circ\text{C}$	[13]

<sup>a</sup> After reaction, additional EtOH was added to sol (C) to adjust the EtOH:Si molar ratio to 22.

S-5200 field emission scanning electron microscope operated at 1 kV. TEM observations of the mesoporous sublayer pore structure was carried out with a JEOL 2010 microscope operated at 200 kV. Grazing incidence small-angle X-ray scattering (GISAXS) analysis of the pore structure of the sublayers was performed in beam line 1-BM of the Advanced Photon Source (APS) facility in Argonne National Laboratory (Argonne, IL).

### 3. Results and discussion

Fig. 1 shows SEM top views of the 100-nm Anodisk surface before (a), and after (b) deposition of the F127-templated mesoporous silica sublayer. As seen from Fig. 1(b), the silica sublayer fills the pore of the support, but the silica material does not cover the surface of the support, in agreement with the cross-sectional TEM shown in Fig. 2(a). In the case of the 20-nm Anodisk coated with a Brij56-templated mesoporous silica sublayer, there was no difference between the surface of the bare and the coated support (image not shown), which suggests that the silica material was deposited inside the pores of the Anodisk. The presence of the silica material though was confirmed by TEM analysis of the powder scraped off the surface of Anodisk, as seen in Fig. 2(b).

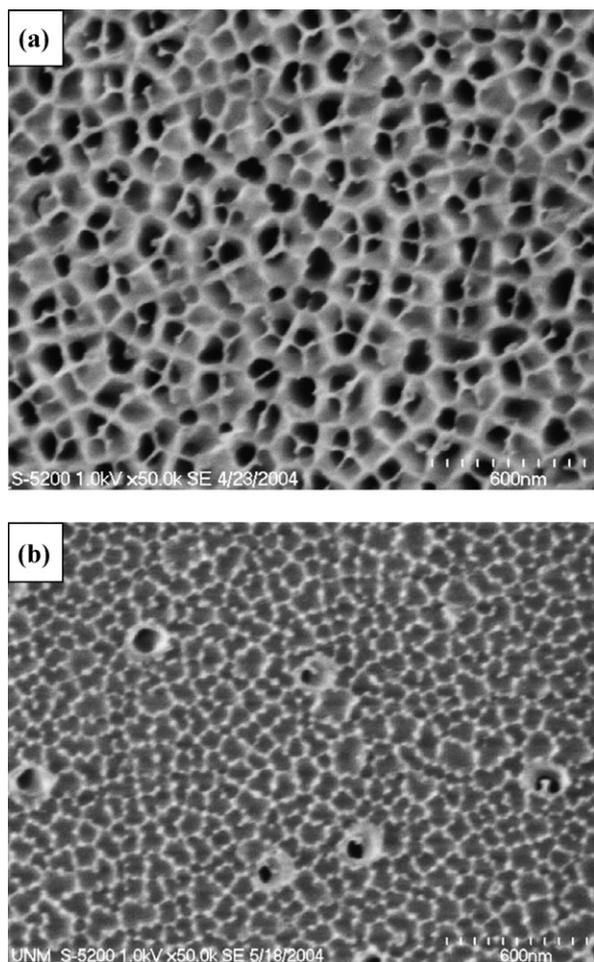


Fig. 1. SEM top view of the 100-nm Anodisk surface before (a), and after (b) deposition of a F127-templated mesoporous silica sublayer using sol composition (B) in Table 1.

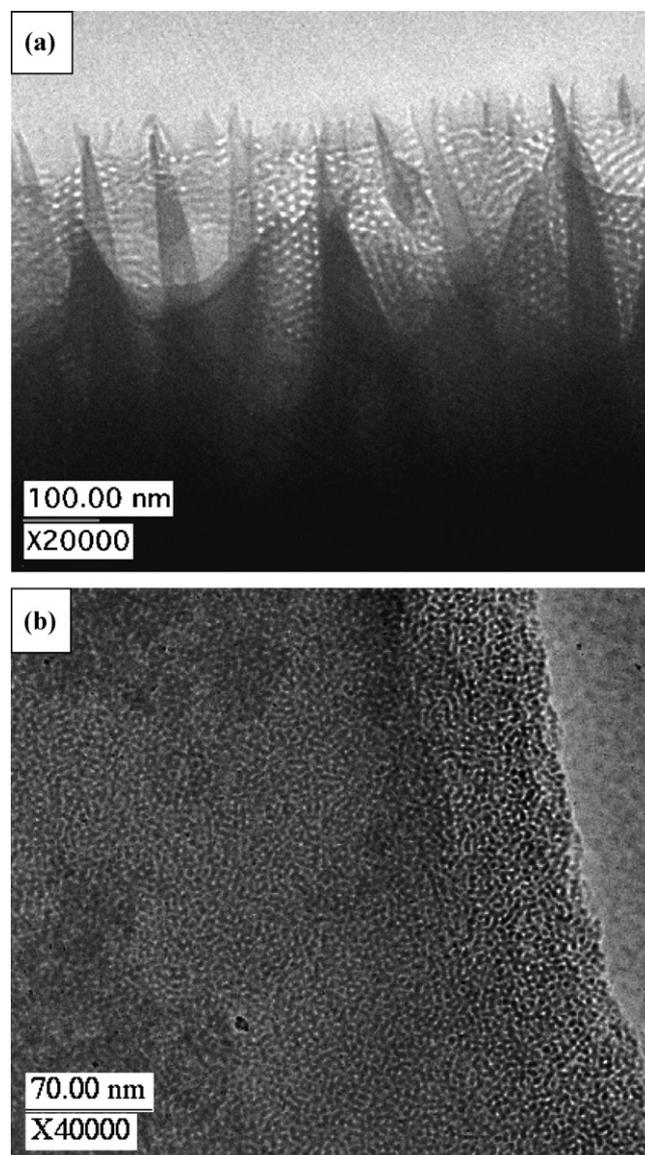


Fig. 2. (a) Cross-sectional TEM micrograph of same sample shown in Fig. 1(b); (b) TEM micrograph of the powder sample scraped off the surface of a 20-nm Anodisk support coated with a Brij56-templated mesoporous silica sublayer using sol composition (A) in Table 1.

The pore size of the Brij56 sublayer was  $\sim 2$  nm [10] while that of the F127 sublayer was 5–6 nm. Further GISAXS analysis of the mesostructure of the F127 sublayer (Fig. 3) revealed a disordered mesophase with average lattice parameter  $d = 14.4$  nm.

Right after deposition and ambient drying ( $100^\circ\text{C}$ , vacuum), both Brij56 and F127 templated sublayers on 20- and 100-nm Anodisks were fairly impervious, as judged by  $\text{N}_2$  permeance in the range 0.01 MPU (versus 600 MPU of the bare Anodisk) measured by transient vacuum permeation. In order to examine whether the sublayers can survive the high-T calcination step to decompose the surfactant, we performed permoporosimetry measurements of the calcined sublayer using ethanol vapor as the pore blocking fluid [10]. Fig. 4 shows the reduction in  $\text{N}_2$  permeance of the 100-nm Anodisk support (a), and a supported F127-templated sublayer (b), as a function of increasing relative

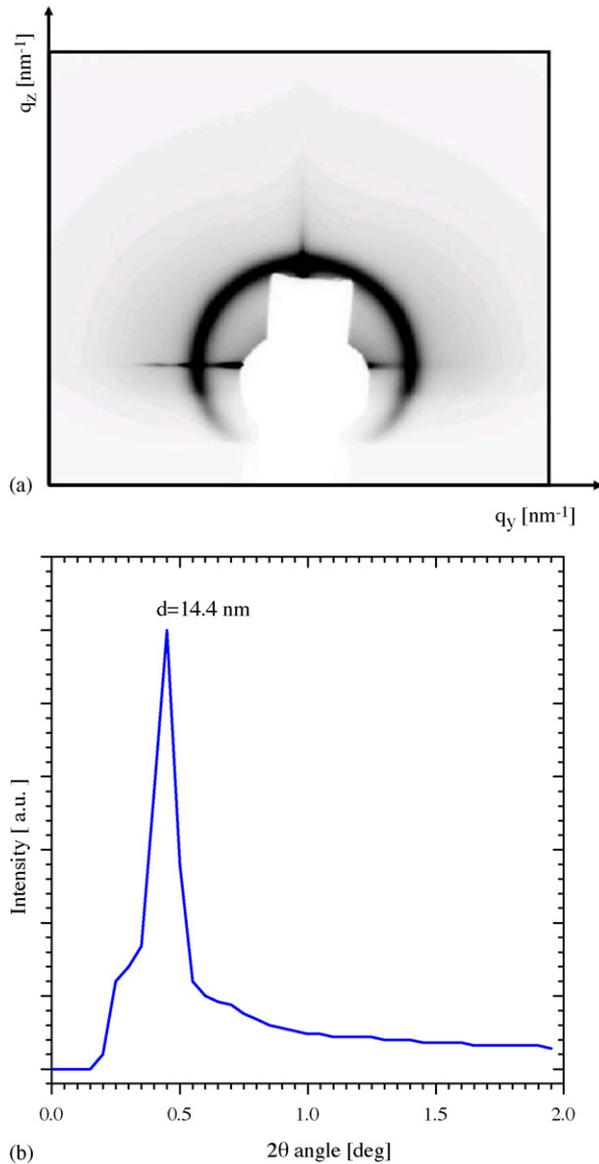


Fig. 3. (a) GISAXS pattern of a F127-templated mesoporous silica sublayer deposited on 100-nm Anodisk support, showing a diffuse ring arising from the disordered mesophase seen in Fig. 2(a); (b) intensity integration of the pattern shown in (a), showing a peak at  $2\theta = 0.5^\circ$ , corresponding to an average  $d$  value = 14.4 nm.

ethanol saturation in both the feed and sweep sides of the membrane. In the case of the bare support, ethanol vapor was not able to block its large (100 nm) pores even at saturation levels of 90%. In the case of the sublayer, a gradual permeance reduc-

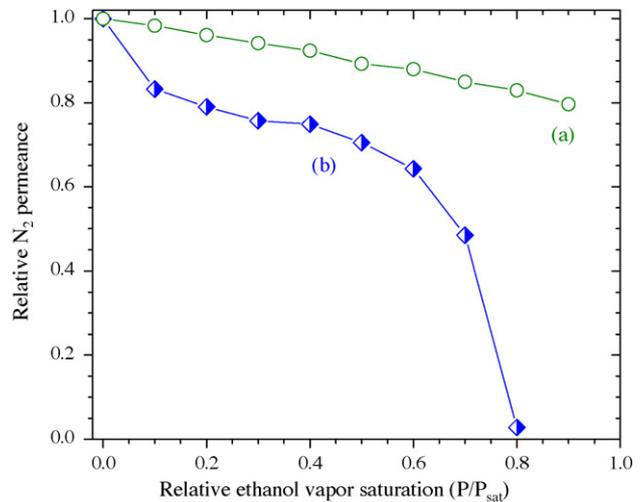


Fig. 4. Permeosimetry test of a 100-nm Anodisk support before (a), and after (b) deposition of a F127-templated mesoporous silica sublayer using sol composition (B) in Table 1. The feed was a  $100 \text{ cm}^3 \text{ (STP) min}^{-1}$  stream of 10 vol.% N<sub>2</sub>-in-He in counter-current flow with a  $100 \text{ cm}^3 \text{ (STP) min}^{-1}$  He stream. The relative ethanol saturation was achieved by splitting  $x$  ( $x = 10\text{--}90$ )  $\text{cm}^3 \text{ (STP) min}^{-1}$  of He through 2 ethanol bubblers before entering the feed and permeate sides of the membrane.

tion down to a level of 3% of the original value is achieved at saturation level of 80%. This suggests that the sublayer is fairly compact although a small number of defects (e.g. microcracks at the silica/alumina interface or unfilled support pores) may be present. These defects could be possibly repaired by repeating the sublayer deposition process, which was not attempted at this stage.

In order to demonstrate the suitability of the mesoporous silica/anodic alumina composite as membrane support for molecular separations, we further deposited a microporous silica membrane using well-established polymeric silica sol protocols resulting in membranes with a molecular cut-off in the range of  $3.5 \text{ \AA}$  [13,16]. Membrane deposition in this case was achieved by spin-coating, since the high-T calcination step used for surfactant decomposition pyrolyzed the supporting polypropylene ring of the Anodisk as well, and hence it was impossible to handle the support from its edge without cracking it.

Table 2 summarizes the room-T CO<sub>2</sub> permeance and binary CO<sub>2</sub>:N<sub>2</sub> separation factors of microporous silica membranes spin-coated on Brij56 and F127 templated sublayers on 20- and 100-nm Anodisk supports, respectively. Both membranes showed comparable CO<sub>2</sub> permeance, but membrane M1 deposited on the 20-nm Anodisk with a Brij56-templated sub-

Table 2  
Binary CO<sub>2</sub>:N<sub>2</sub> permeation properties at 25 °C of microporous silica membranes deposited on 20- and 100-nm Anodisk supports with Brij56 and F127-templated silica sublayers, respectively

Sample	Support	Sol recipe (sublayer/membrane)	CO <sub>2</sub> permeance (MPU) <sup>a</sup>	Separation factor [CO <sub>2</sub> :N <sub>2</sub> ]
M1	20-nm Anodisk	A and C	2.9	84
M2	100-nm Anodisk	B and D	2.7	47

The feed was a 10:90 (v/v) binary CO<sub>2</sub>:N<sub>2</sub> mixture.

<sup>a</sup> 1 MPU =  $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ .

layer showed improved CO<sub>2</sub>:N<sub>2</sub> selectivity. This result suggests that fewer defects are present in the small-pore Anodisk/silica composite, and hence the overlying gas separation membrane is of higher quality. In both cases however, the CO<sub>2</sub>:N<sub>2</sub> separation factor was superior to that reported by other researchers [16,17], suggesting that the anodic alumina/mesoporous silica composite is a better support compared to conventional macroporous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with a mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> top-layer.

Finally, in order to demonstrate the role of the mesoporous sublayer in membrane formation, we spin-coated the microporous silica membrane directly on a bare 20-nm Anodisk support without sublayer. In that case, the anodic alumina/silica composite showed Knudsen-type selectivity for CO<sub>2</sub> and N<sub>2</sub> transport, suggesting that the sublayer plays a crucial role in securing a continuous overlying microporous membrane.

#### 4. Conclusions

A new and simple processing scheme combining traditional sol–gel chemistry and surfactant-assisted self-assembly has been successfully implemented in order to deposit microporous gas separation silica membranes on commercially available, inexpensive and high-flux anodic alumina supports. The results of this work imply that in order to successfully fill large support pores by one (or multiple) dip-coating steps, a proper choice of surfactant should be made so that the sublayer pore size is a suitable average (e.g. the geometric one) of that of the support and the final membrane. The proposed processing scheme can also be extended for development of other types of inorganic membranes based on zeolites, pyrolytic carbon or dense metals provided that anodized metal oxide supports of proper thermal and chemical stability are identified.

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