

## Characterization of anisotropic UF-membranes: top layer thickness and pore structure\*

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(Received October 29, 1989)

### Abstract

Anisotropic poly(2,6-dimethyl-, 1,4-phenylene oxide) (PPO) ultrafiltration membranes are characterized by means of two techniques. A new method for the determination of skin thicknesses, the gold sol method, is introduced and applied to these membranes. The membranes appeared to have a well-defined skin with a thickness of 0.2  $\mu\text{m}$ . The results were combined with permporometry, a method that measures the size of the active pores that are actually responsible for the membrane performance. By following this approach it is possible to calculate the porosity of the skin layer and to obtain a suitable prediction of the pure water flux.

*Keywords:* ultrafiltration membrane, anisotropic; poly(2,6-dimethyl-, 1,4-phenylene oxide) membrane; skin thickness; pore size; porosity; gold sol method; permporometry

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### Introduction

In commercial separation processes anisotropic membranes are preferentially used because of their high efficiency. Such membranes consist of a very layer, the toplayer or skin, and a supporting layer. In anisotropic UF-membranes the small pores in the thin, relatively dense toplayer are responsible for the separation characteristics of the membrane and the open sublayer is supposed not to influence the membrane performance. The size distribution of the pores present in the skin determines the selectivity of the membrane whereas the skin thickness is an important parameter which co-determines the permeability of the membrane.

Pore-size distributions of anisotropic UF-membranes can be measured using several independent methods like thermoporometry, gas adsorption-desorp-

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\*Paper presented at the 6th International Symposium on "Synthetic Membranes in Science and Industry", Tübingen, September 4–8, 1989.

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tion hysteresis, bubble pressure measurements and permoporometry. These quite sophisticated methods allow the measurement of pore sizes in the range of several nanometers to tens of nanometers. Only when a combination of these techniques is used, a better insight in the pore morphology of the membrane is possible. However, for a better understanding of the relation between the morphology of a membrane and transport through this membrane, more knowledge of the characteristics parameters of the membrane, like the thickness of the skinlayer and the size of the open pores in the skin is needed.

In this paper two quite new characterization techniques are applied. Firstly, a new technique for the determination of the skin thickness of anisotropic UF-membranes is presented. This technique is combined with a second technique: permoporometry a method that is developed to determine the pore size and pore-size distribution of the active pores in the top layer of the membrane. The results obtained from the combined techniques were used to calculate essential characteristics of poly(2,6-dimethyl-, 1,4-phenylene oxide) (PPO) ultrafiltration membranes.

### **The determination of skin thicknesses: the gold sol method**

#### *Principle*

Although the thickness of an anisotropic membrane is a very important characteristic parameter, there are only few methods available to measure this thickness. In most cases the skin thickness of the membrane is estimated by means of scanning electron microscopy (SEM). The size of the pores in the skin, however, is too small to be distinguished with SEM and often a certain gradient in pore size from the top of the skin towards the porous sublayer exists. In the case of anisotropic ultrafiltration membranes made by phase inversion the determination of the skin thickness is hardly possible and the analysis is limited to a rough estimation.

The new method presented here is based on the penetration of colloidal particles of a well-known size and a very narrow size distribution into the macroporous sublayer of an anisotropic UF-membrane. The particles entering from the macroporous sublayer side, will penetrate in the porous support until small pores near or in the skin are reached. When the pore size is smaller than the particle size the particles will get stuck. When the particles used are only slightly larger than the pores in the skin, a thin layer not permeated by colloids is formed. The thickness of this layer can be measured by applying scanning electron microscopy (SEM) in two different modes. More information about pore sizes in the sublayer can be obtained by comparing experiments done with different colloidal gold solutions, containing particles of an increasing size.

## Experimental

### *Preparation and analysis of the gold colloids*

The size of the particles is dependent on the conditions during synthesis [1]. In this paper two monodisperse sols with different mean particle size, 6 nm and 50 nm, were used. Colloidal solutions containing particles with a mean diameter of 6 nm were synthesized in the following way: 10.0 ml 1.0 wt.% solution of chloroauric acid ( $\text{HAuCl}_4$ ) was added to 1000 ml water (filtered by reverse osmosis) and the pH of the solution was adjusted to a value of 7.2 with 0.1 M  $\text{K}_2\text{CO}_3$  solution. The solution was heated to boiling in a reaction vessel and 10.0 ml diethylether saturated with white phosphorus (at 20°C) was added to the well-stirred solution. Then the solution was cooled down and, in order to remove the excess of unreacted phosphorus, a stream of air was lead through the red solution during one night. Sols containing particles with a mean size of 50 nm were made by adding a 10.0 ml 1.0 wt.% sodium citrate solution to a boiling solution of 1000 ml water (purified by reverse osmosis) and 10.0 ml 1.0 wt.% chlorauric acid. During the reaction the solution was stirred vigorously until the color was red. After five minutes the solution was cooled down. All chemicals used were of analytical grade and supplied by Merck.

The prepared sols were characterized using transmission electron microscopy (TEM, Jeol 200 CT) and particle size distributions were determined by counting particles and measurement of their cross-section by means of image processing.

### *Membrane preparation and permeation*

Membranes investigated were poly(2,6-dimethyl-, 1,4 phenylene oxide) (PPO) membranes. PPO membranes were prepared from a 10 wt.% polymer solution in a mixture of trichloroethylene and octanol-1 in a weight ratio 78/22. The solution was cast at room temperature to a thickness of 0.20 mm on a glass plate and the films were coagulated in a methanol bath. All solvents used were of analytical grade.

The membranes were placed with the skin side down in an Amicon cell (membrane area 38.5 cm<sup>2</sup>) and permeated at 1 bar with RO-water for at least 30 min. Then a small amount of the dark red colloidal gold solution was added to enter the membrane from the porous side. The colloidal gold solution, containing 100 ppm gold, was permeated through the membrane at 1 bar. In all cases a colorless permeate was obtained, indicating that retention was at least 99%. The amount of solution used was adjusted in order to obtain a detectable layer in the membrane: in case of 6 nm particles 100 ml sol solution, in case of 50 nm particles 200 ml solution was needed. For each membrane only one type of colloidal solution, with 6 nm or 50 nm particles, was used.

### *Scanning electron microscopy*

Cross-section electron micrographs were obtained with a Jeol JSM 35 CF scanning electron microscope using both the secondary electron image (SEI) and the backscattered electron image (BEI) mode. Micrographs made in the SEI mode are essentially topographical, the rough morphological structure can be examined. The backscattered mode yields not only topographical but also analytical information about the specimen. In the BEI mode the contrast depends on the atomic number of the materials present in the membrane: the gold particles are detected as light areas in the dark polymer matrix. The skin thickness appears as a dark area between trapped gold particles and a sputtered gold layer on top.

Dry membrane samples were prepared by immersion of the wet membrane for 15 min in a 50/50 (w/w) ethanol/water bath and another 15 min in a pure ethanol bath, upon which the membrane was dried at room temperature in a vacuum chamber. A thin gold layer ( $\sim 30$  nm) was sputtered on top of the membrane. Again the pores of the membrane were filled with ethanol and fractured at liquid nitrogen temperature. Only in this way a cross-section with a sharp fracture can be obtained. The sample was dried as described before. To prevent the sample from charge-up while performing electron microscopy it was covered with a coal layer by using a Balzers BSV 202 coal evaporation unit.

### **Results**

TEM micrographs of the colloidal solutions are given in figures 1(a) and (b). The distribution of the sol with the smaller particles is asymmetric and

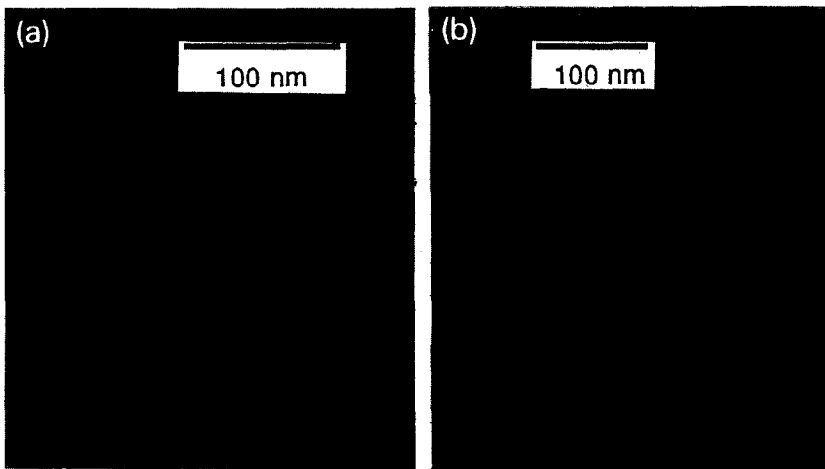


Fig. 1. Typical transmission electron micrographs of colloidal gold solutions. (a) mean diameter: 6 nm; (b) mean diameter: 50 nm.

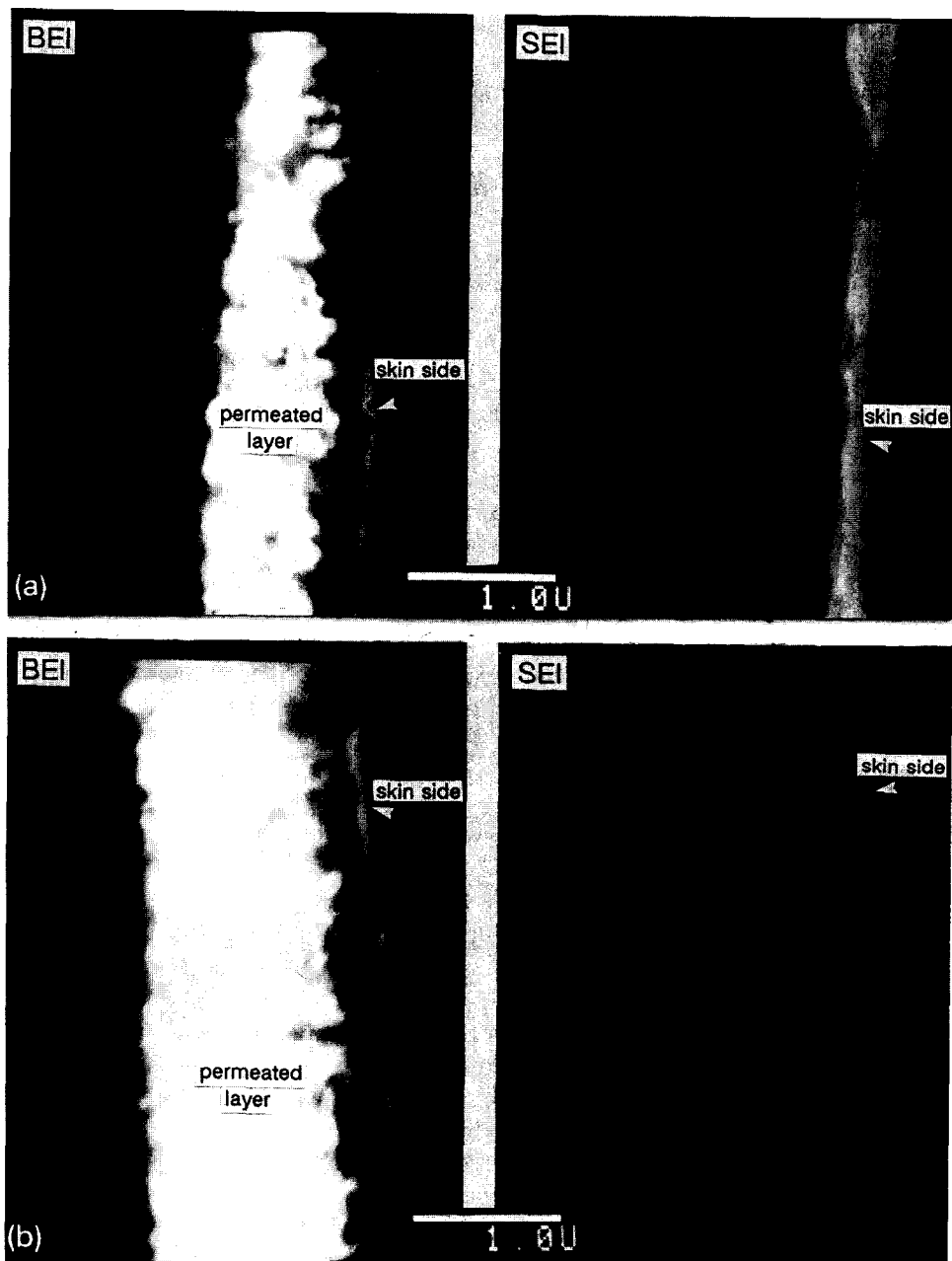


Fig. 2. Cross sections of PPO membranes permeated with gold sols containing particles with a mean diameter of 6 nm (a), and 50 nm (b), using electron microscopy; BEI (left hand side) and SEI (right hand side).

very sharp; 72% of the particles have diameters between 5.6 and 6.4 nm. Particles with diameters smaller than 5.6 nm are not present. The sol with the larger particles has a more Gaussian distribution. In this case the mean particle diameter is 50 nm with a standard deviation of 5 nm [2].

Figures 2(a) and (b) show cross-sections of PPO membranes treated with colloid solutions containing particles with a mean diameter of 6 nm and 50 nm respectively. The electron microscope is used in the “normal”, secondary image (SEI) mode and the backscattered (BEI) mode. The right hand side of the picture shows the membrane in the SEI mode. It can be seen that the sample is fractured very sharply, as is essential for a correct interpretation of the picture. The presence of gold can be detected very well in the backscattered mode (BEI, left hand side of figures 2(a) and (b)). Although the individual particles can not be detected, the edge formed by these permeated particles can be seen clearly. In the BEI mode, three layers can be recognized: a thin light line resulting from the sputtered gold on top of the membrane, a more diffuse layer caused by the penetrated particles and in between the (dark) skin layer in which the pores are smaller than the sol particles.

When a PPO membrane is treated with a sol, containing particles of 6 nm, an impenetrable layer with a thickness of about  $0.2 \mu\text{m}$  is detected. Using a sol with particle size 50 nm the thickness of the toplayer is varying between 0.2 and  $0.3 \mu\text{m}$ , a very small increase compared to the experiments where 6 nm particles were used. This indicates that PPO membranes have a very well-defined skinlayer thickness, with a pore size very much different from the pores in the macroporous layer underneath.

### **Determination of the active pore sizes: permoporometry**

#### *Theory*

Permporometry is one of the few techniques available, capable of measuring the distribution of the active pores present in the skin of an anisotropic membrane. Active pores are the pores exclusively related to the performance of the membrane. Permporometry combines the classical method used for the characterization of catalysts, i.e. gas adsorption-desorption hysteresis [3,4], with the so-called counterdiffusion measurements, frequently used in theoretical approaches of transport mechanisms through porous beds [5].

The principle of our method is given in Fig. 3. It is based on the counterdiffusion of two gases, nitrogen and air present in stream 1 and 2 respectively, in the absence of an absolute pressure gradient. The driving force for transport is a concentration gradient of oxygen and the diffusive transport is measured as an increased oxygen concentration in stream 1. The condensable gas, methanol, is used at a uniform relative vapor pressure all over the system. The relative vapor pressure of methanol determines the number of available open pores for oxygen diffusion.

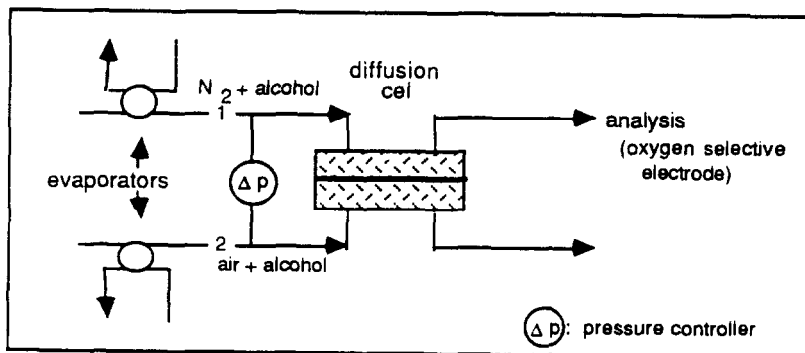


Fig. 3. Permpermometry: experimental set-up; explanation see text.

The determination of pore sizes available is based on the well-known phenomenon of capillary condensation of a liquid inside a porous medium. The vapour pressure of the condensed liquid in a capillary pore depends on the curvature of the liquid-gas interface and can be described by the Kelvin relation (1).

$$\ln p_r = -2\gamma v \cos\theta / RTr_k \quad (1)$$

In our experiments the contact angle of  $\theta$  of methanol on the pore walls is assumed to be zero.

Although not strictly defined, it is generally agreed that for pores smaller than 1.5 nm, the Kelvin equation is no longer valid. This is conceivable because in these very fine pores, with about the size of a few molecules, the concept of meniscus becomes meaningless [3]. From adsorption-desorption hysteresis studies it is known that during capillary condensation, the pore walls are covered with an adsorbed film, having a thickness  $t$ . Thus the adsorption and desorption processes are not occurring in the pore itself, but in a pore with an adsorbed layer, i.e. in the "core". Consequently the Kelvin relation leads to values of the "core" radius or Kelvin radius ( $r_k$ ) instead of the pore radius ( $r_p$ ). The radius of the pore  $r_p$  is found from the relation:

$$r_p = r_k + t \quad (2)$$

in which  $t$  is the thickness of an adsorbed layer of the condensable gas.

As a consequence of the counterdiffusion approach, there should be no mechanical pressure drop across the membrane and both sides of the membrane are flushed with the gas-vapor mixture. These are the main differences between our technique and the methods published in literature [6,7]. The advantages are twofold: firstly the equilibrium between the vapor and the liquid in the capillaries is reached much faster (ca. 30 min). Secondly, the driving force for the counterdiffusion of the gas is a concentration gradient, so a well-

defined diffusion regime is present and consequently in mesoporous structures model calculations are relatively simple.

Since transport is related directly to the open, active pores with radii generally in the order of nanometers, it can be assumed that the diffusion is of the Knudsen type. In case of a capillary model this can be described by eqn. (3).

$$J_k = \{\pi n r_k^2 D_k \Delta p_{\text{gas}}\} / \{RT \tau l\} \quad (3)$$

$$D_k = \{0.66 r_k (8RT/\pi M)\} \quad (3a)$$

## Experimental

Starting from a relative methanol pressure ( $p_r$ ) equal to 1, which means a minimum in diffusional transport, the membrane is equilibrated at a known relative vapor pressure ( $p_r < 1$ ). At the same time the diffusional flux of oxygen through the membrane is measured with an oxygen selective electrode. In this way a desorption isotherm is obtained, given in terms of oxygen flux (as a measure of the open pores) at various relative pressures of methanol. From this curve the active pore-size distribution can be calculated by using eqns. (1)–(3).

## Results and discussion

### *The thickness of the adsorbed t-layer*

A, for PPO membranes, typical plot of the diffusive flux vs. the relative vapor pressure is shown in Fig. 4. Using relation (1) the Kelvin radius ( $r_k$ ) is calculated from the relative vapor pressure. The number of pores is calculated from the experimental flux values (using eqn. 3). To calculate the real pore radius ( $r_p$ ), the Kelvin radius has to be corrected for the adsorbed  $t$ -layer (eqn. 2). In

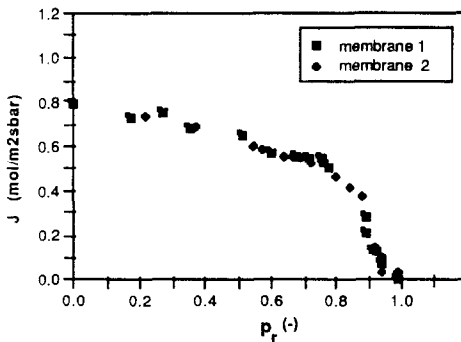


Fig. 4. Diffusional oxygen flux as function of relative vapor pressure during desorption, for 2 different membrane samples (the samples were both made from the same polymer solution; in the permeability experiments, methanol was used as the condensable gas).



classical adsorption studies this thickness is calculated from separate adsorption experiments which are performed using homogeneous non-porous surfaces [3]. This approach is very laborious and therefore we used an approximation to calculate the  $t$ -layer directly from the permoporometry data.

The validity range of the Kelvin equation,  $1.3 \text{ nm} < r_k < 50 \text{ nm}$ , corresponds with relative vapor pressures of  $0.60 < p_r < 0.99$ . From Fig. 4 it can be seen that the flux is increasing rapidly upon lowering  $p_r$  (below  $p_r \sim 0.9$ ) and up to  $p_r = 0.6$  the flux is growing relatively fast. At lower relative pressures the flux does increase, but not very much. It can be argued that in the range of relative pressures between 0.99 and 0.6 capillary desorption takes place: the flux increases because of an increasing number of open pores. At lower relative pressures only the  $t$ -layer in the open pores desorbs, so the pore size available for transport becomes somewhat larger and again the flux increases. When it is assumed that the flux increase at lower relative pressures ( $p_r \leq 0.6$ ) is only due to the desorption of the  $t$ -layer and that in all the pores present the  $t$ -layer and that in all the pores present the  $t$ -layer thickness is equal we can calculate this thickness ( $t$ ) using eqns. (2) and (3). At the relative pressure of 0.6 the pore size available for transport is  $r_k$  and when the  $t$ -layer has been totally desorbed (at  $p_r = 0$ ) the effective pore size is  $r_p = r_k + t$ . So starting from the experimental flux values found in Fig. 4 at  $p_r = 0.6$  and  $p_r = 0$  and using eqns. (2) and (3), the value  $r_p (= r_k + t)$  for each pore can be calculated and hence  $t$  is obtained. Of course this method yields only a quite rough estimation of the  $t$ -layer thickness, but since in the case of PPO membranes larger pores are determining the performance of the membrane, it is sufficient to know that this thickness  $t$  is very small. For methanol, the condensable gas used here, in this way a  $t$ -layer thickness of 0.25 nm was found, a value that agrees fairly well with data in literature [4].

#### *Combination of gold sol method and permoporometry*

In order to calculate the number of pores in the membrane skin all characteristic parameters in eqn. (3) are needed. Using the gold sol method, the skin thickness has been determined to 0.2  $\mu\text{m}$  and assuming a tortuosity factor in the membrane of one, the number of pores can be estimated. The result is shown in Fig. 5. From the number of pores and their sizes the surface porosity of the membrane is calculated to be 0.5%, a very low value, as is found also for other UF-membranes [8].

In order to check the applicability of the parameters found, a "theoretical" pure water flux of the membrane was calculated, using the Poiseuille equation (4).

$$J_{\text{aq,th}} = (\pi n r^4 \Delta p) / (8 \mu l) \quad (4)$$

From this equation a pure water flux is calculated to range from 13–46 l/hr-

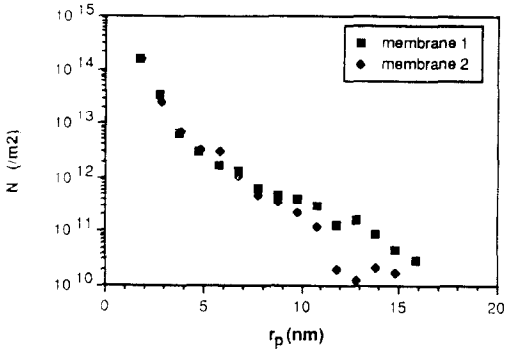


Fig. 5. Size distribution of the interconnected pores in two samples of PPO membranes (same two samples as in Fig. 4).

m<sup>2</sup>-bar, for different PPO membranes (but all made from the same polymer solution). Experimental water fluxes varied between 15 and 80 l/hr-m<sup>2</sup>-bar. The fact that theoretical and experimental pure water fluxes are of the same order of magnitude indicates that the characteristic parameters of the membrane found by means of permporometry in combination with the gold sol method can describe the transport through the membrane to a reasonable extent.

## Conclusions

With the gold sol method the thickness of the skinlayer of anisotropic poly(2,6 dimethyl-, 1,4 phenylene oxide) (PPO) membranes has been determined at 0.2  $\mu\text{m}$ . Combining this method with permporometry, a method that measures the active pore-size distribution, leads to a better understanding of the relation between pore morphology and transport through UF-membranes. The skin porosity is calculated to be 0.5%. From the results obtained with both methods the pure water flux can be predicted appropriately.

## List of symbols

$p_r$	relative vapour pressure (-)
$\gamma$	surface tension (N/m)
$v$	molar volume (m <sup>3</sup> /mol)
$\theta$	contact angle (°)
$r_k$	Kelvin radius (m)
$\tau$	tortuosity (-)
$l$	skin thickness (m)
$M$	molar mass permeating gas (g/mol)
$\Delta p_{\text{gas}}$	partial pressure gradient of oxygen (N/m <sup>2</sup> )

$J_k$	diffusive flux (mol/m <sup>2</sup> )
$n$	number of pores (/m <sup>2</sup> )
$r_k$	Kelvin radius (m)
$D_k$	Knudsen diffusion coefficient (m <sup>2</sup> /sec)
$\mu$	viscosity (kg/m-sec)
$\Delta p$	pressure gradient (N/m <sup>2</sup> )

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