

# Nanostructure of a High-Permeability, Hydrogen-Selective Inorganic Membrane

S. T. Oyama, D. Lee, P. Hacıoğlu, Y. Gu, R. F. Saraf

Virginia Tech, Dept. of Chemical Engineering, Blacksburg, VA, USA, oyama@vt.edu

## ABSTRACT

This paper describes the preparation and properties of an inorganic membrane with permeability for H<sub>2</sub> comparable to palladium and with over 99.9% selectivity over larger species like CO, CO<sub>2</sub> and CH<sub>4</sub>. The membrane is a composite formed by the deposition of a thin, 20 nm SiO<sub>2</sub> layer on an alumina support. The alumina support is obtained by the deposition of a boehmite sol on top of a porous substrate, so as to create a uniform structure with small pore sizes. The permeation of the small gas species, H<sub>2</sub>, He, and Ne through the silica layer is analyzed in detail in order to obtain insight about the transport mechanism and the structure of the silica. The order of permeance through the silica layer is highly unusual, He > H<sub>2</sub> > Ne, following neither molecular weight nor size. The order of permeation is quantitatively explained using a statistical mechanics approach, which takes into consideration the density of solubility sites for the various species and the vibrational frequency of the species within the sites. An extension of the Masaryk-Fulrath treatment for glasses combined with the Percus-Yevick model is used to estimate the vibrational frequency ( $7.0 \times 10^{12} \text{ s}^{-1}$ ), solubility site density ( $3.0 \times 10^{26} \text{ m}^{-3}$  for H<sub>2</sub>) and the average distance between sites (0.84 nm). This is the first time an inorganic membrane has been described in detail at the nanometer level.

**Keywords:** silica/alumina membrane, hydrogen permeation, statistical mechanics theory, solubility sites

## 1 INTRODUCTION

Silica-based membranes have been studied extensively because of their excellent properties in selective hydrogen permeation. The first membranes were obtained [1,2,3] by placing silica inside the pores of Vycor glass substrates using reactive chemical vapor deposition (CVD). In a subsequent development it was found that better results were obtained by placing the silica on the outer surface of the substrate to form a thin compact layer [4]. Until recently the mechanism of hydrogen permeation through silica membranes has not been studied in detail. In this paper we develop the theory of gas permeation through the silica layer building upon an existing description for vitreous silica glasses [5]. A key aspect of the existing theory is the presence of solubility sites for the permeating species. In this work we calculate the distance between solubility sites using the Percus-Yevick treatment for a

dense liquid, which assumes it is composed of random, non-interacting spheres.

The order of permeance through the silica layer is highly unusual, He > H<sub>2</sub> > Ne, following neither molecular weight nor size. This is the same order as observed in vitreous silica glass, but occurs with lower activation energies in the silica layer. The order of permeation is explained for the first time using a statistical approach, which takes into consideration the density of solubility sites for the various species and the vibrational frequency of the species within the sites.

The membranes are generally prepared by chemical vapor deposition of a silica precursor at low temperatures using H<sub>2</sub>O, O<sub>2</sub> or O<sub>3</sub> as co-reactants. This work describes the preparation of a special highly hydrogen permeable silica membrane, referred to as Nanosil, obtained by an adaptation of the method. Instead of using low temperatures, the SiO<sub>2</sub> layer is deposited at high temperatures by thermal decomposition. This gives rise to a composite membrane with excellent selectivity ( $\sim 10^3$ ) for the small gas molecules (He, Ne and H<sub>2</sub>) over other larger gas molecules (CO<sub>2</sub>, CO, and CH<sub>4</sub>).

## 2 EXPERIMENTAL

The silica/alumina membrane was prepared by depositing a thin silica layer on a porous  $\gamma$ -alumina support by the thermal decomposition of tetraethylorthosilicate (TEOS) at 873 K in an argon stream. The membrane support used in this study was purchased from US Filter (Part No. S700-0011), and had a tubular geometry with an outside diameter of 10 mm and a thickness of 1.5 mm. This membrane support had a multi-layered structure consisting of a coarse  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> tube coated with finer layers of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and an inner top layer of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of average 5 nm pore size. A 4 cm section of the alumina membrane support was connected at both ends to two pieces of dense alumina tubing using a high temperature glass glaze (Duncan, IN, Part No. 1001). Gas tight connections between the membrane support and the dense tubing were obtained after 0.5 h of thermal treatment at 1150 K.

After the joint connection, an additional  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer was introduced on top of the existing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer of the alumina support to reduce defects or pinholes that give rise to a low hydrogen selectivity in the silica layer. A 0.05 M dispersion of boehmite ( $\gamma$ -AlOOH) sol was prepared

following the method reported by Uhlhorn [6]. Aluminum tri-sec-butoxide (Aldrich, 97%) was added to boiling water with vigorous stirring, and 0.07 mole  $\text{HNO}_3$  per mole butoxide was added. This colloidal solution was boiled until most of the butanol was evaporated, then was refluxed for 20 h. Polyvinylalcohol (PVA, Fluka, M.W. 72000) solution was prepared separately by adding 3.5 g of PVA to 100  $\text{cm}^3$  of boiling water followed by 5  $\text{cm}^3$  of 1 M  $\text{HNO}_3$ . The PVA solution was then refluxed for 4 h. A final 0.05 M boehmite sol was prepared after adding 660  $\text{cm}^3$  of the PVA solution per mol of boehmite followed by stirring for 3 h at 353 K. The alumina support tubing was dip coated with the 0.05 M boehmite sol for 10 s, dried for 24 h at room temperature, and then calcined at 873 K for 24 h (heating rate 1  $\text{K min}^{-1}$ ).

For the CVD of the silica layer, the alumina support substrate was installed concentrically inside another piece of glass tubing of 14 mm inside diameter using machined Swagelok fittings with Teflon ferrules. After placing the assembly in an electric furnace, argon gas flows were introduced on the outer shell side (19  $\mu\text{mol s}^{-1}$ ) and inner tube side (15  $\mu\text{mol s}^{-1}$ ) of the reactor (flow rates in  $\mu\text{mol s}^{-1}$  may be converted to  $\text{cm}^3 \text{min}^{-1}$  (NTP) by multiplying by 1.5), and the temperature was raised to 873 K. A flow of tetraethylorthosilicate (TEOS, Aldrich, 98%) was introduced on the inside of the porous alumina substrate using a bubbler (at 298 K) with argon (4  $\mu\text{mol s}^{-1}$ ) as a carrier gas. This stream was mixed with the tube stream of argon before introducing it to the tube side to produce a stream with a TEOS concentration of 0.02  $\text{mol m}^{-3}$  (0.045 mol %). The synthesis of the silica membrane was studied by varying the silica deposition time. The CVD process was interrupted at various times and the permeance of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  were measured at different deposition times at 873 K.

General gas permeation measurements were conducted in the temperature range of 373 – 873 K by flowing 40  $\mu\text{mol s}^{-1}$  of a pure gas at 160 kPa through the inner tube. The permeation rate of each gas exiting from the shell side of the reactor assembly was measured with a sensitive bubble flow meter at atmospheric pressure. The permeance of gas was obtained from the expression  $Q_i = F_i / A \Delta P_i$ , where  $Q_i$  is the permeance ( $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ) of species  $i$ ,  $F_i$  is the gas flow rate on the shell side ( $\text{mol s}^{-1}$ ),  $A$  is the surface area ( $\text{m}^2$ ) of the membrane section, and  $\Delta P_i$  is the pressure difference (Pa) between the shell and tube side. For higher sensitivity the permeance of the gases was also measured with a gas chromatograph (GC) equipped with a thermal conductivity detector (SRI, Model 8610B). The tube side gas flow rates and pressure conditions were the same as above, however, on the shell side an argon flow was introduced as a sweep gas for the permeated gas. The shell side outlet gas flow rate was measured using a bubble flow meter, and the flow was injected into the GC to obtain the concentration of the permeated gas. The permeance was then calculated using the outlet gas flow rate and the concentration of the permeated gas on the shell side.

### 3. RESULTS and DISCUSSION

The evolution of the gas permeance on the silica membrane was measured at 873 K as a function of the silica deposition time to monitor the formation of the silica layer on the membrane support. The results are shown in Fig. 1.

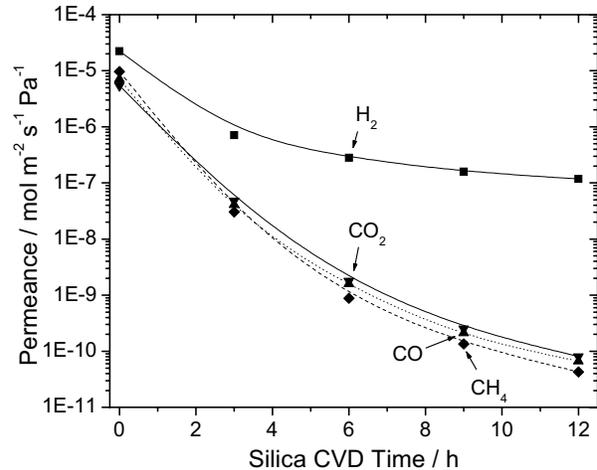


Figure 1. Gas permeance vs. silica deposition time.

Initially, the fresh alumina support showed very high permeance for all of the gases ( $\text{H}_2 = 2.2 \times 10^{-5}$ ,  $\text{CH}_4 = 9.7 \times 10^{-6}$ ,  $\text{CO} = 7.1 \times 10^{-6}$ ,  $\text{CO}_2 = 5.4 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ). The permeance of all the gases decreased with silica deposition time. For hydrogen, the permeance decreased rapidly after 3 h of silica deposition to the order of  $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , and then decreased slowly with further silica deposition. In contrast, the permeance of  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  showed a continuous and rapid drop with silica deposition. After 12 h of deposition the permeance of hydrogen remained at  $1.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , whereas the permeance of the other gases dropped off significantly ( $\text{CH}_4 = 4.3 \times 10^{-11}$ ,  $\text{CO} = 6.7 \times 10^{-11}$ ,  $\text{CO}_2 = 8.0 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ). The results indicate that a complete silica layer was formed on the alumina support after 12 h of deposition, and that the layer was selective for  $\text{H}_2$  transport while significantly excluding passage of  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  through the membrane. Before the silica deposition, the permeance order of the gases through the alumina support was  $\text{H}_2 > \text{CH}_4 > \text{CO} > \text{CO}_2$  showing an inverse dependence on the molecular weight of the gases, in agreement with the Knudsen diffusion mechanism. However, after 3 h of silica deposition the permeance order changed to  $\text{H}_2 > \text{CO}_2 > \text{CO} > \text{CH}_4$ , which followed molecular size ( $\text{H}_2 = 0.289 \text{ nm}$ ,  $\text{CO}_2 = 0.33 \text{ nm}$ ,  $\text{CO} = 0.376 \text{ nm}$ ,  $\text{CH}_4 = 0.38 \text{ nm}$  [7]), and this order was retained with further silica deposition. This gives evidence that the mechanism of molecular differentiation by the silica layer is through size selectivity.

The hydrogen selectivity over other gases is shown as a function of hydrogen permeance in Fig. 2. The selectivity for hydrogen on the fresh alumina support was low for all the gases. The selectivity was characteristic of Knudsen

diffusion. After 3 h of silica deposition the selectivity for hydrogen showed a slight increase accompanied by a large decrease in H<sub>2</sub> permeance from the order of 10<sup>-5</sup> to 10<sup>-7</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>. The H<sub>2</sub> selectivity then increased rapidly with further silica deposition, with only a small drop in hydrogen permeance. After 12 h of silica deposition the hydrogen selectivity of the membrane increased to over 1000 for all the gases (CH<sub>4</sub>: 2800, CO: 1800, CO<sub>2</sub>: 1500). This is a purity above 99.9 %.

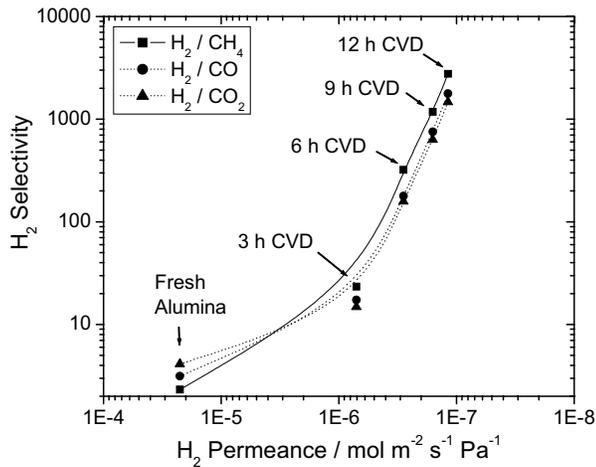


Figure 2. Selectivity of hydrogen vs. H<sub>2</sub> permeance.

The temperature dependence of small gas transport through the silica membrane obtained after 12 h of silica deposition was investigated by measuring the permeance of He, H<sub>2</sub> and Ne at various temperatures (373 – 873 K). It was found that the permeance of these gases through the silica membrane was activated, and increased with temperature. This differed from the permeance in the fresh alumina membrane support where the permeance decreased with temperature in accordance with the Knudsen transport mechanism.

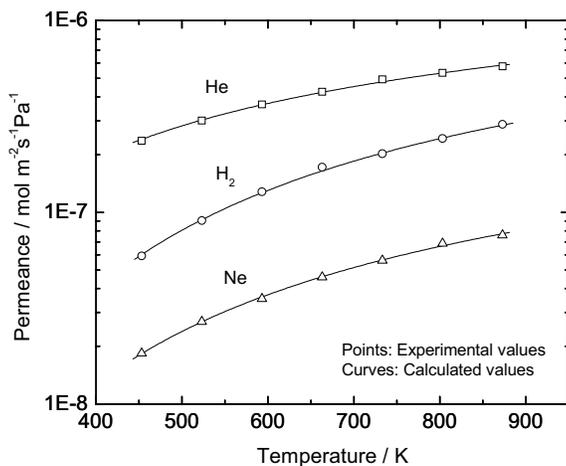


Figure 3. Theoretical and Experimental Permeance Curves.

The permeance order of these gases was unusual

$$\text{He} > \text{H}_2 > \text{Ne}$$

as it did not follow the size (He = 0.26 nm, H<sub>2</sub> = 0.289 nm, Ne = 0.275 nm [7]) nor the mass of the species (He = 4.0 au, H<sub>2</sub> = 2.01 au, Ne = 20.1 au).

The results can be explained [8] using an equation originally derived to describe permeability of monatomic gases in vitreous glass that was based on a mechanism involving jumps between solubility sites [5]. The equation used a classical statistical mechanics approach [9] and assumed equilibrium sorption in the sites [10], random motion, and a transition state with two degrees of vibrational freedom and one degree of translational freedom. For the case of hydrogen this equation needs to be adapted to account for the partial loss of rotational degrees of freedom as the molecule passes through the doorways.

$$Q = \frac{1}{6L} \left( \frac{d^2}{h} \right) \left( \frac{h^2}{2\pi m k T} \right)^{\frac{3}{2}} \left( \frac{\sigma h^2}{8\pi^2 I k T} \right)^{0.2} \frac{(N_s/N_A)}{(e^{h\nu^*/2kT} - e^{-h\nu^*/2kT})^2} e^{-\Delta E_K/RT} \quad (1)$$

In this equation  $Q$  is the permeance of a gas,  $L$  is the thickness of the membrane,  $d$  is the jump distance,  $m$  is the mass of the species,  $h$  is Planck's constant,  $k$  is Boltzmann's constant,  $\nu^*$  is the vibrational frequency of the species in the doorways between the sorption sites,  $T$  is temperature,  $N_s$  is the number of solubility sites available per m<sup>3</sup> of glass volume,  $N_A$  is Avogadro's number,  $R$  is the gas constant, and  $\Delta E_K$  is the activation energy for hopping between sorption sites. For non-monatomic gases  $\sigma$  is the symmetry number of the permeating species, with  $\sigma = 2$  in the case of hydrogen, and  $I$  is the moment of inertia. The results are shown in by the curves in Fig. 3. As can be seen, very good fits are obtained to the experimental points.

A concern about the application of the permeability equation (1) is the use of an arbitrary jump distance. The jump distance should not be an independent parameter, but should be the average distance,  $d$ , between the sites. If the sites do not interact and are non-overlapping (i.e., the sites are subject to an excluded volume interaction), then  $d$  should only be a function of number density,  $N_s$  and diameter of the sites,  $\sigma$ .

A collection of randomly distributed sites embedded in a solid may be treated as an assembly of hard spheres that are mutually impenetrable and have no interactions. This is a situation that can be addressed by the Percus-Yevick treatment in the theory of liquids, where the spheres represent the atoms of the liquid. The representation of an amorphous solid as a liquid is appropriate as both have only short range order [11].

Considering that the sites are non-interacting and may not overlap, only the short-range correlations will be important. This is called the Percus-Yevick (PY) approximation. For the case of hard spheres, the direct correlation function  $C(k)$ , can be calculated analytically using the PY approximation [12] given in the next page.

$$C(k) = 4\pi \int_0^\sigma \frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{6\eta(1+\frac{1}{2}\eta)^2}{(1-\eta)^4} \frac{r}{\sigma} \frac{\eta(1+2\eta)^2}{2(1-\eta)^4} \frac{r}{\sigma}^3 \frac{\text{Sin}(kr)}{kr} r^2 dr \quad (2)$$

where, the  $\sigma$  is the diameter of the site and  $\eta = \pi N_s \rho \sigma^3 / 6$  is the volume fraction occupied by the sites. Details will be given in a future publication [13].

Although analytical solutions for the radial distribution function and its derivatives are available [14], these still involve infinite sums and are cumbersome to use. In this work the radial distribution function is calculated numerically

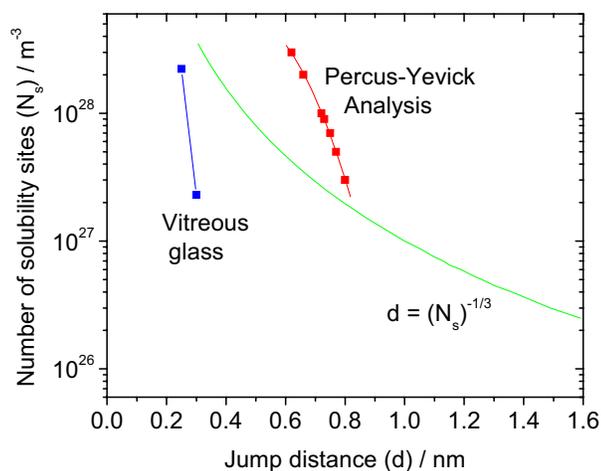


Figure 4. Relationship between number of solubility sites and jump distance

The figure compares values used in the vitreous glass literature, the P-Y calculation results, and the prediction for a random array of points  $(N_s)^{-1/3}$ . It can be seen that the jump distances used in the description of vitreous glass are the smallest, even smaller than the predictions from the array of points of zero volume, which is impossible. These previously used jump distances are consequently in error. The jump distances calculated by the P-Y treatment are larger than those predicted by the array of points, as they should be for a collection of sites of finite diameter. In this case the size of the solubility sites was taken to be 0.3 nm, which is what is expected for both the glass and the silica membranes.

Using these results and fitting the experimental results (Fig. 3) to equation (1) gives the following values of the parameters. The numbers are physically realistic.

Table 1. Parameters in equation (1).

Species	He	H <sub>2</sub>	Ne
$v$ (s <sup>-1</sup> )	5.3x10 <sup>12</sup>	7.0x10 <sup>12</sup>	2.7x10 <sup>12</sup>
$N_s$ (m <sup>-3</sup> )	4.7x10 <sup>26</sup>	3.0x10 <sup>26</sup>	4.0x10 <sup>26</sup>
$\Delta E_K$ (kJ mol <sup>-1</sup> )	8.0	13.8	16.6

## REFERENCES

- [1] W. G. Perkins, D. R. Begeal, "Diffusion and permeation of He, Ne, Ar, Kr, and D<sub>2</sub> through silicon oxide thin films", *J. Chem. Phys.* 54, 1683, 1971.
- [2] T. Okubo, H. Inoue, "Introduction of specific gas selectivity to porous glass membranes by treatment with tetraethoxysilane", *J. Membr. Sci.* 42, 109, 1989.
- [3] G.R. Gavalas, C.E. Megiris, S.W. Nam, "Deposition of H<sub>2</sub>-permselective SiO<sub>2</sub> films", *Chem. Eng. Sci.* 44, 1829, 1989.
- [4] A.K. Prabhu, S.T. Oyama, "Highly hydrogen selective ceramic membranes: application to the transformation of greenhouse gases", *J. Membr. Sci.* 176, 233, 2000.
- [5] J.S. Masaryk, R.M. Fulrath, "Diffusivity of helium in fused silica", *J. Chem. Phys.* 59, 1198, 1973.
- [6] R.J.R. Uhlhorn, M.H.B.J. Huis In't Veld, K. Keizer, A. J. Burggraaf, "Synthesis of ceramic membranes, Part I. Synthesis of non-supported and supported  $\gamma$ -alumina membranes without defects", *J. Mater. Sci.* 27, 527, 1992.
- [7] D.W. Breck, "Zeolite Molecular Sieves: Structure, Chemistry and Use", Wiley, New York, 636, 1974.
- [8] D. Lee, S. T. Oyama, "Gas Permeation Characteristics of a Hydrogen Selective Supported Silica Membrane", *J. Membr. Sci.* 210, 291, 2002.
- [9] R. M. Barrer, D. E. W. Vaughan, "Solution and Diffusion of Helium and Neon in Tridymite and Cristobalite", *Trans. Faraday Soc.* 63, 2275, 1967.
- [10] P.L. Studt, J. F. Shackelford, R. M. Fulrath, "Solubility of gases in glass-a monatomic model", *J. Appl. Phys.* 41, 2777, 1970.
- [11] J. M. Ziman, "Models of Disorder", Cambridge Univ. Press, Cambridge, 87, 1979.
- [12] C.A. Croxton, "Introduction to Liquid state Physics", John Wiley & sons, New York, 84, 1975.
- [13] S. T. Oyama, D. Lee, P. Hacarlioglu, R. F. Saraf, In preparation for *J. Membr. Sci.*
- [14] J. Largo, J.R Solana, "A simplified analytical expression for the first shell of the hard-sphere fluid radial distribution function", *Fluid Phase Equil.* 167, 21, 2000.

The authors acknowledge the Director, National Science Foundation, Division of Chemical and Thermal Systems for award of Grant No. CTS-0321979 in support of this work. The authors also thank the ConocoPhillips Company for their sponsorship of the research program.