

CO₂ sorption of a ceramic separation membrane

Herbert Wormeester*, Nieck E. Benes, Gerald I. Spijksma, Henk Verweij, Bene Poelsema

MESA + Research Institute, University of Twente, Enschede, The Netherlands

Abstract

The ellipsometric characterization of the CO₂ sorption of a silica membrane provides a fast and accurate technique for the characterization of maximum sorption and the heat of adsorption. Both parameters are evaluated for the 73 nm thick silica layer as well as the 1650 nm thick supporting γ -layer. The applicability of ellipsometry for studying sorption of supported membranes relies on a careful analysis of the membrane prior to sorption measurements.

© 2004 Elsevier B.V. All rights reserved.

Keywords: CO₂ sorption; Silica membrane; Ellipsometry

1. Introduction

The sorption of gases in a porous medium has various applications in the range of gas separation and gas detection. Silica membranes with a pore size comparable to the kinetic size of molecules can be used as sieves, e.g. for natural gas purification, molecular air filtration, selective CO₂-removal and industrial H₂-purification [1]. Such porous silica material can be produced via a sol–gel method. Oxidized porous silicon has larger pores and is used in the realisation of so-called optical noses. These devices were demonstrated to have sensitivity in the low parts per million region of several alcohols [2]. The use of silica has the advantage that the membranes can be used at relatively high temperatures.

The use of silica membranes in gas purification requires a low resistance to transport of small (fast) molecules, i.e. a very thin membrane. Such a thin, defect-free layer can be achieved by dip-coating silica onto a multi-layered porous alumina support structure, for example a nano-porous γ -alumina layer on top of an α -alumina layer. The γ -layer provides a smooth surface with sufficiently small pores to enable the formation of a silica layer from sol particles, while the α -layer provides mechanical strength. Information about the sorption behaviour of different gases in the micro-porous material is imperative for a proper description of its separation performance. Due to the small dimensions of the membrane layers these properties are not easily

measured by standard macroscopic techniques, such as volumetric and gravimetric sorption measurements. Measuring the properties of unsupported ‘bulk’ material can circumvent this problem. Although this is frequently done to investigate the effect of changes in the sol–gel process for the synthesis of the membranes, the properties of supported and unsupported silica are generally not identical. Ellipsometry provides a technique that enables the characterization of supported silica membranes in an accurate and relatively fast way.

2. Optical characterisation of the membrane

Before the sorption of CO₂ can be measured, a careful characterization of the membrane is required. As all layers are dielectrics, only $\tan(\psi)$ can be measured accurately with a rotating polarizer ellipsometer. To reduce the number of independent fit parameters, first the γ -alumina layer on top of the α -alumina is measured. After this, the membrane is coated with a silica layer and ellipsometrically characterized. The difference between the measurement with and without the silica layer is used for determining the optical properties of the silica layer.

The details of the preparation of the α -alumina substrate from pure alumina powder as well as the dip coating procedures for the application of the γ -alumina layer from boehmite sol (γ -AlOOH) and the dip coating of silica layers from silica sol is described elsewhere [3].

Before the membrane can be characterized, it is outgassed in vacuum (<1 mBar) by heating it above

*Corresponding author. Tel.: +31-53-489-3148.

E-mail address: h.wormeester@utwente.nl (H. Wormeester).

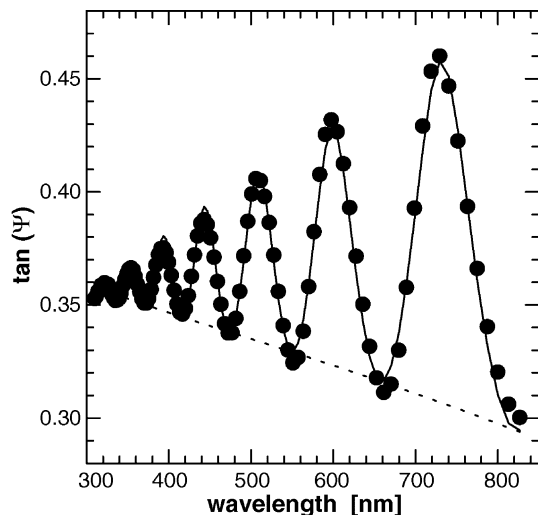


Fig. 1. Wavelength dependence of $\tan(\Psi)$ for γ -layer on top of an α -layer, dots: experimental data, line: fit of the optical model using a Cauchy relation for modelling both layers.

200 °C with a 50 W halogen lamp mounted behind the membrane. Especially water is removed in this process. Ellipsometry measurements were made with a home made rotating polarizer ellipsometer. It consists of a 75 W Xe lamp, two Glan-Taylor polarizers, a monochromator and a photo-multiplier. The angle of incidence of the light beam was 70°. The time dependent behaviour of the ellipsometric parameters was recorded every 2 s. Fig. 1 shows the measured spectrum of the γ - and α -alumina layer. As a model for the refractive index of both alumina layers, a Cauchy series was used that mimics both optical absorption in the UV as well as in the IR region, although no absorption of the incident light is noted in the wavelength region used.

$$n^2 = c_0 + c_1/\lambda^2 + c_2\lambda^2. \quad (1)$$

The thickness of the γ -layer was measured to be 1.654 μm with a numerical accuracy of 2 nm. This value corresponds well with SEM measurements of these layers. The values of the coefficients used in Eq. (1) for both alumina layers are given in Table 1.

After dip coating the silica layer and out gassing of the membrane structure the additional silica layer was also modelled with a similar Cauchy formula. The thickness of the silica layer was found to be 73 ± 1 nm. This thickness is in good agreement with values obtained from SAM and XPS argon sputter profiles (60–100 nm) [4]. Intermixing at both the α - and γ -alumina interface and the γ -alumina and silica interface cannot be excluded. The analysis of the ellipsometric spectra with just a sharp interface between the three layers suffices for a good fit. Additional parameters describing intermixing are thus not justified.

Table 1
Dispersion coefficients of the different layers

	α -alumina	γ -alumina	silica
c_0	1.914	1.803	1.805
c_1 (nm^2)	-6.39E3	1.015E4	2.17E3
c_2 (nm^{-2})	5.02E-7	3.09E-8	2.05E-7

Fig. 2 shows the experimentally determined dispersion curves for the three materials in the membrane. The α -alumina support is macro-porous with pore size >50 nm. It is thus not expected that a simple effective medium approximation can be used to evaluate the porosity of this layer as both shape and pore size distribution will effect the dispersion. The pores in the γ -alumina layer are only several nanometers large and an effective medium approximation like Bruggeman's theory [5] can be applied. With sapphire as the dielectric function of one medium and vacuum of the other, a porosity of 51% is found. A slightly higher porosity (55–60%) was reported for unsupported γ -alumina by N_2 adsorption/desorption measurements [4]. The silica layer has pores with sub nanometer size, but the optical properties of dense silica layers are unknown. Quite often the optical properties of quartz are used instead. Comparing the measured dispersion of the silica layer to that of quartz, see Fig. 2, the use of quartz representing dense silica, would result in a wavelength dependent porosity. Quartz can thus not be used as a substitute for dense silica layers. This is probably due to the large amount of OH groups present in the silica layer, which provide extensive absorption in the IR region. An average porosity of 20% can be evaluated. This value

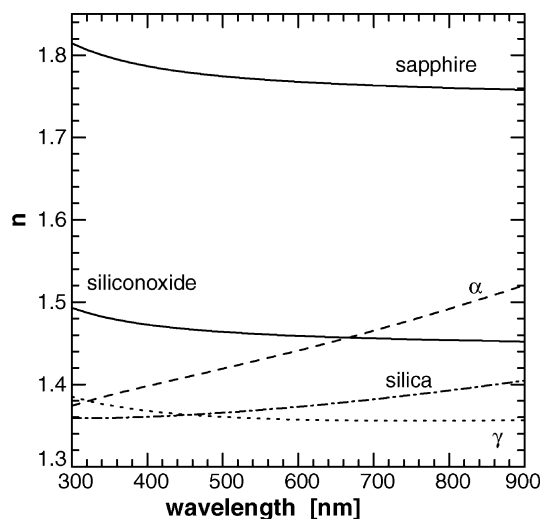


Fig. 2. Experimentally determined dispersion of the various layers of the membrane. Also shown are the dispersion curves of sapphire and quartz.

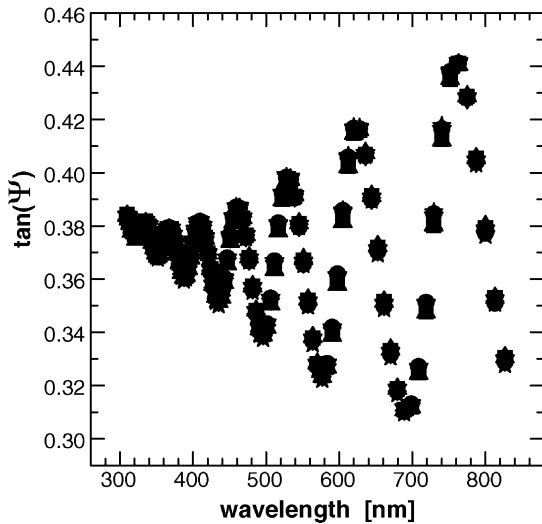


Fig. 3. Ellipsometry measurements under vacuum condition measured at 0 °C (■), 10 °C (▲), 25 °C (▼), 35 °C (●) and 45 °C (★). The five curves are equivalent and no temperature dependence of the refractive index can be observed.

agrees with measurements on both supported and unsupported silica membranes [6].

The sorption measurements are performed at temperatures in the range from 0 to 45 °C. For the analysis of the sorption measurements, it is essential that the temperature dependence of the refractive index of the ceramic materials used is known. Fig. 3 shows $\tan(\psi)$ at various temperatures under vacuum conditions. The indiscrimination of the various signals shown indicates that the outgassed membrane material does not show a temperature dependent refractive index in the temperature range considered.

3. CO₂ sorption measurements

Fig. 4 shows the time response of $\tan(\psi)$ upon the exposure and evacuation of the membrane to CO₂. At first the CO₂ pressure is 2 bar and the sample is cooling down. This results in an increase of the amount of CO₂ sorbed. The temperature is controlled by an oil bath surrounding the glass pressure cell that is connected to a thermostat. Temperature changes are always performed at a pressure of 2 bar CO₂. This ensures that the gas inside the pressure chamber will get the same temperature as the surrounding wall in direct contact with the oil bath. The membrane in turn will get the same temperature as the gas. Changing the gas pressure by evacuating the pressure cell leads to a fast change in $\tan(\psi)$. Letting in the CO₂ again leads to a reversible change in $\tan(\psi)$ and no hysteresis behaviour is observed. The response time for evacuating is approximately 7 s, while exposure to CO₂ is a little faster. These response times are related to the gas inlet and

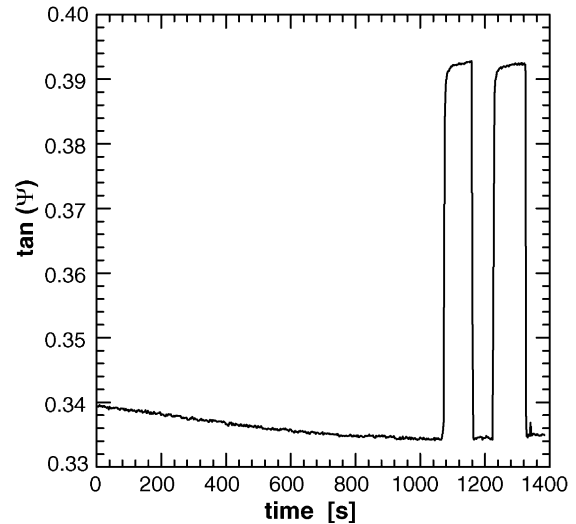


Fig. 4. Time dependence of the ellipsometric signal, wavelength 608 nm, with the membrane at 0 °C and switching the CO₂ pressure from 2 bar – 0 bar – 2 bar – 0 bar – 2 bar. The initial decrease of the signal is due to the settling to the measurement temperature at a pressure of 2 bar.

evacuation set-up. The actual response time of the membrane is faster.

The wavelength dependence of $\tan(\psi)$ for both the unloaded membrane and for various CO₂ pressures at a temperature of 0 °C is shown in Fig. 5. The change in $\tan(\psi)$ upon loading could be accounted for by modification of the dielectric functions of the silica and the γ -layer. The adjustment of the dielectric functions is related to the presence of polarizable CO₂ molecules. Because the interactions between CO₂ and the inorganic

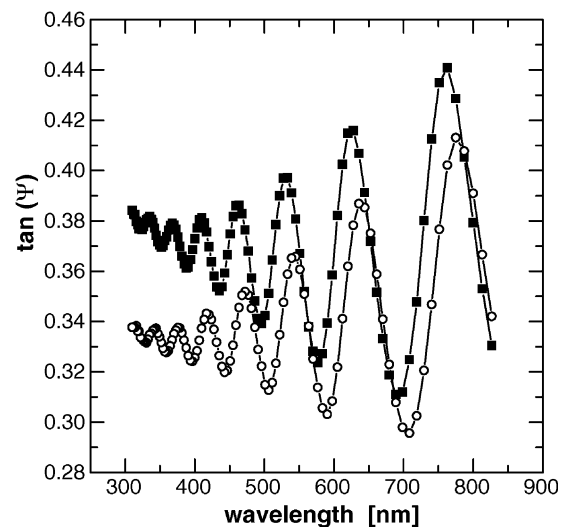


Fig. 5. Effect of CO₂ sorption on $\tan(\psi)$, in the three-layered membrane system at a temperature of 0 °C. Squares denote spectrum under vacuum condition, open circles spectrum after exposure to CO₂ at 2 bar.

materials are only weak, the optical properties of the adsorbed CO₂ molecule are taken similar to those of free CO₂ molecules, which have a polarizability of $\alpha = 3.02 \times 10^{-40}$ F/m at a wavelength of 500 nm, with only a slight dispersion [7]. This polarizability gives for N molecules a dielectric function $\varepsilon_{\text{CO}_2}$, with ε_0 the permittivity of vacuum

$$\varepsilon_{\text{CO}_2} = \frac{1 + N \frac{2\alpha}{3\varepsilon_0}}{1 - N \frac{\alpha}{3\varepsilon_0}} \quad (2)$$

The change in the dielectric function of the layers due to the presence of CO₂ will only be small, and hence a linear relation between the change in dielectric function of the layer $\delta\langle\varepsilon\rangle$ and the number of molecules N can be assumed. The number of molecules N has to be multiplied by the occupied fraction of the layer, to obtain the density of molecules in the layer N_g .

$$\delta\langle\varepsilon\rangle = CN_g\alpha/\varepsilon_0 \quad (3)$$

The value of the parameter of proportionality, C , has to be calculated with the aid of an effective medium theory. The effective medium comprises three components; the solid inorganic material, the CO₂ molecules and the unfilled pores, i.e. vacuum. This value lies between one and $\langle\varepsilon\rangle\langle\varepsilon\rangle$. The three components Bruggeman gives with ε_m the dielectric function of the non-porous material

$$C = \frac{1}{f} \frac{(3f-1)\langle\varepsilon\rangle + \varepsilon_m}{2\langle\varepsilon\rangle + \varepsilon_m/\langle\varepsilon\rangle} \quad (4)$$

This value of C can be easily applied for the determination of the CO₂ content of the γ -alumina layer. However, both the porosity of the silica layer and the dielectric properties of the non-porous silica layer, i.e. ε_m are unknown. This problem can be avoided by using Lichteneckers logarithmic mixing rule [5]

$$\ln\langle\varepsilon\rangle = \sum_i f_i \ln\varepsilon_i \quad (5)$$

This results in $C = \langle\varepsilon\rangle$.

Fig. 6 shows CO₂ sorption isotherms as evaluated for four different temperatures, with using the value of C as given by Lichteneckers mixing rule.

4. Langmuir behaviour

The simplest model for describing the sorption behaviour is the Langmuir model. The lines in Fig. 6 denote

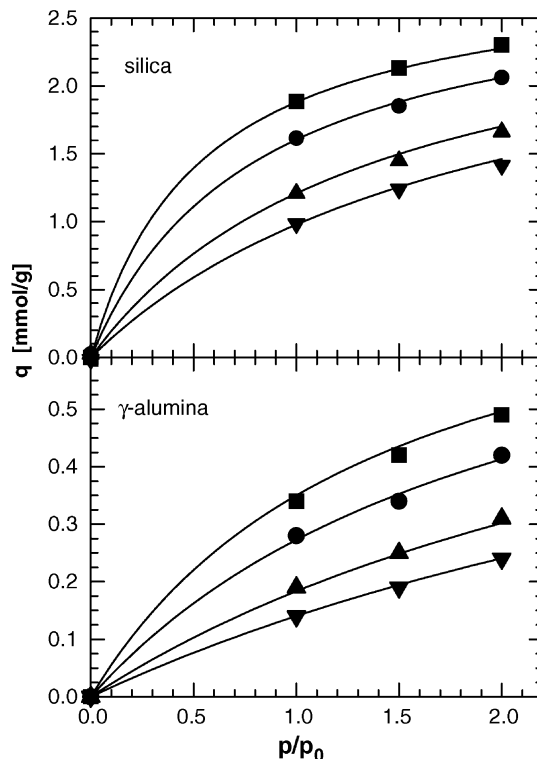


Fig. 6. CO₂ isotherms for both the silica and γ -alumina thin layer, $p_0=1$ bar at 0 °C (■), 10 °C (●), 25 °C (▲) and 35 °C (▼). The lines are Langmuir isotherms fitted to the data.

Langmuir isotherms fitted to the measured data, with A , a temperature dependent constant and p and p_0 , the pressure of CO₂ and the reference pressure of 1 bar.

$$\theta = \frac{q}{q_0} = \frac{Ap/p_0}{1 + Ap/p_0} \quad (6)$$

This provides a maximum sorption q_0 of 0.84 mmol/g for the γ -layer and 2.4 mmol/g for the silica layer. For unsupported silica, a maximum sorption capacity of 2.7 mmol/g was found using a gravimetric high-pressure sorption set-up [8]. The shape of the isotherms is also quite similar to those found with a low-pressure volumetric set-up. Note that for unsupported silica layers the pore density and the pore size is not similar to the supported material. However, it certainly shows that ellipsometry is capable of providing a realistic absolute number of molecules CO₂ in the porous material.

The saturation coverage is used to evaluate the relative occupancy θ . The linear relation, Eq. (3), assumed between CO₂ sorption and the change in refractive index and confirmed by the Langmuir isotherms implies that by using the occupancy the heat of adsorption can be evaluated without the influence of the specific effective medium approximation used for evaluating C . The heats of sorption are determined from an Arrhenius plot, see

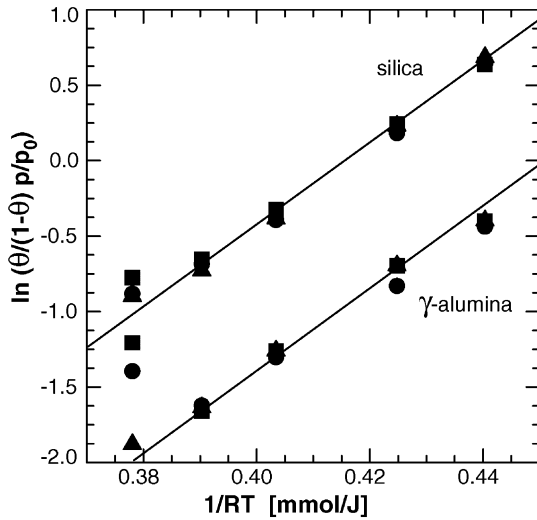


Fig. 7. Arrhenius plot of the amount of CO₂ normalized to the pressure in both the silica and γ -alumina layer. The data shown is for pressures of $0.5p_0$ (■), $1p_0$ (●) and $2p_0$ (▲).

Fig. 7, and are 24.6 ± 1.0 and 27.0 ± 1.3 kJ/mol for the γ -alumina and silica layer, respectively.

The heat of sorption of γ -alumina has been the subject of several studies. Auroux and Gervasini [9] reported a heat of sorption for physisorbed CO₂ on commercial γ -alumina of 25 kJ/mol. Uhlhorn reported a heat of sorption of unsupported γ -alumina that was prepared in a similar manner as our layers of 26 kJ/mol [10]. These values and the one found in this research indicate that the adsorption of CO₂ on supported and unsupported γ -alumina is very similar.

The heat of sorption for unsupported silica was found to be 24 kJ/mol [8]. The value of this heat of sorption is indicative for physisorption. The difference in value for supported and unsupported silica is probably due to the difference in pore size and pore morphology. The

increased heat of sorption for the supported material could thus imply a smaller pore size, i.e. smaller than 4–5 Å. This agrees well with the noted absence of methane permeance (kinetic diameter 3.8 Å) for supported silica, while for unsupported silica methane sorption can be observed.

5. Conclusion

Ellipsometry was shown to be an accurate and versatile tool for the characterisation of gas sorption in very thin ceramic membranes. Comparatively fast the absolute value of sorbed CO₂ was evaluated for an alumina silica membrane structure. The optical characterisation allows the possibility of evaluating a large range of pressure and temperature. The sorption behaviour is well described with Langmuir isotherms and both the maximum sorption capacity and the heat of sorption for both the γ -alumina and the silica layer are compatible to those obtained for unsupported material.

References

- [1] R.M. de Vos, H. Verweij, *Science* 279 (1998) 1710.
- [2] G. Wang, H. Arwin, *Sens. Actuators B.* 85 (2002) 95.
- [3] N.E. Benes, Ph.D. Dissertation, University of Twente (2000) ISBN 90-36515327 (<http://www.ub.utwente.nl/webdocs/ct/1/t0000027.pdf>).
- [4] R.S.A. de Lange, J.H.A. Hekkink, K. Keizer, A.J. Burggraaf, *J. Membrane Sci.* 99 (1995) 57.
- [5] D.A.G. Bruggeman, *Ann. Physik.* 24 (1935) 636.
- [6] C.J. Brinker, G.W. Sherer, *Sol–Gel Science: the Physics and Chemistry of Sol–Gel processing*, Academic Press, Boston, 1990.
- [7] L. Bornstein, *Zahlenwerte und Funktionen aus Physik – Chemie – Astronomie – Geophysik – Technik*, Auflage 6 Band 2 Teil 8 (1962).
- [8] R.S.A. de Lange, J.H.A. Hekkink, K. Keizer, A.J. Burggraaf, Y.H. Ma, *J. Porous Mat.* 2 (1995) 141.
- [9] A. Auroux, A. Gervasini, *J. Phys. Chem.* 94 (1990) 6371.
- [10] R.J.R. Uhlhorn, Ph.D. Thesis, University of Twente (1990).