Contents lists available at ScienceDirect





Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Gas concentration polarization and transport mechanism transition near thin polymeric membranes



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ARTICLE INFO

Concentration polarization

Keywords:

Transition flow

Vapor deposition

Porous polymer

Ultra-thin membrane

ABSTRACT

Advanced material engineering gave rise to cutting-edge characteristics of sustainable separation by fabrication of high permeable and gas selective membranes. A developed fabrication process of ultrathin polymers with controlled microporosity helps understanding pore size dependent transport and performance of thin membranes with constant pore number from continuum to free-molecular to solution-diffusion regimes. Fabrication of polymer layers with controlled pore size was realized by stage-wise physical vapor deposition of dimethylsiloxane oligomers onto porous alumina support. Single process step forms high permeable porous films of 13 nm in thickness. Further deposition allows fabrication of up to 120 nm nanopore-free uniform layers with defined gas selectivity. Permeances as high as 1300 GPU through gas-selective, uniform dense films results in gas concentration polarization and apparent selectivity loss, so far only observed for porous materials. Our fabrication process enabled observation of two unseen separation regimes in the transport physics transition from (nano) channel flow to solution diffusion supported by mathematical model derived for transport through ultra-thin membranes.

1. Introduction

Recent advances in the synthesis of polymer nanofilms and nanoporous polymer materials enabled higher separation performance, in particular, higher permeance in the membrane-based processes desired for energy efficient and sustainable separation [1,2]. Dense, thin and defect-free polymer films are often fabricated via interfacial polymerization [3], and layer-by-layer deposition [4], while mesoporous materials can be prepared via block copolymer phase-separation [5], self-assembly [6] or using porous templates [7-10]. Despite several decades of sustained research and development on such polymeric membranes, transport and separation mechanism has not been yet clearly understood for gas mixture separation in the transition from nanoporous to dense thin film regime. To date, technical challenges in controlling the pore size from several nanometers to sub-nanometers as well as the density and uniformity of pores in polymer thin films have greatly hindered researchers from addressing this subject of research [11-13].

Here we report a synthetic approach to fabricate polymeric nanofilms with controllable microporosity. We employed a stepwise physical vapor deposition (PVD) technique to deposit conformal polymer films on the nanoporous alumina templates. The size of the pores shrinks proportionally with the number of deposition cycles of the polymer until the pores are completely blocked and a continuous film forms. During this process the density and uniformity of the pores are maintained. These features are highly advantageous for the comparative study of the gas transport in polymer films with various pore sizes. Through systematic experiments evaluating membrane performance for single gas transport and gas mixture separation, we observe a clear transition of the transport mechanism between (nano) channel flow and polymer solution-diffusion mechanism. This behavior is further supported by a mathematical model derived specifically for the transport through the thin materials with a consideration of thickness dependent permeability, a property which stays constant for the relatively thick membranes [14,15]. Our results reveal the effect of concentration polarization on up to 16% loss in the gas selectivity even in the case of dense nanopore-free polymer thin film. This observation was predicted before theoretically [16]. But up to now experimental prove could not be realized due to the employment of low permeable membranes. For these membrane materials gas concentration polarization is negligible owing to the significantly smaller permeance compared to the diffusivity of the gas above the membrane. However, with the horizon of high permeable membranes, it is important to consider that these selective layers are unavoidably subject to the selectivity deterioration. We use our high permeable membrane platform to demonstrate the kinetic dependence of the separation performance and emphasize the

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https://doi.org/10.1016/j.memsci.2018.08.070

Received 2 May 2018; Received in revised form 5 August 2018; Accepted 31 August 2018 Available online 01 September 2018 0376-7388/ © 2018 Elsevier B.V. All rights reserved.

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Fig. 1. (a) Schematic of the PVD setup for the vapor deposition of oligomers on the porous alumina support. (b) TEM image from the lamella cross-section of the porous AAO template covered with the polymer. The intruded polymer has a black contrast to the adjacent AAO and the top layer PDMS. The image is taken after gas experiment tests. Inset: SEM top view of the template pores covered with the polymer. The polymer film remains translucent to the electron-beam. (c) AFM surface roughness measurement of the AAO template covered with the polymer. Inset: template surface topography after 12 cycles deposition and complete coverage with the polymer over 1 μ m² area. (d) Estimated pore size distribution of porous polymer after *m* deposition calculated from the deposition modeling. Inset: proposed mechanism of polymer growth at the template channel tip for three steps deposition. The layers correspond to polymer layer after each step. Template pore shrinks upon deposition of each layer (e). Thickness measurement of the deposited polymer (PDMS) on the reference alumina. ALD deposited alumina (AL) has ca. 50 nm thickness on the silicon (Si) substrate.

importance of developing strategies for gas mixing to make full use of highly permeable membranes in the gas separation process.

2. Fabrication

The polymeric membranes with controlled pore sizes and film thickness are synthesized by a cyclic deposition of vaporized dimethylsiloxane (DMS) oligomers on the anodized alumina membrane (AAO) with the average 11 nm wide pores placed at low-temperature region in a heated vacuum chamber (Fig. 1a, Supplementary 1). As vapor diffusion into a high aspect ratio structure is very limited, DMS oligomers mostly condense and form a conformal thin entangled polymer layer (polydimethylsiloxane (PDMS)) at the topmost surface and the channel wall near the pore entrance. Limited intrusion depth originates from higher probability of vapor collision to the nanochannel wall at high vacuum (high Knudsen number) than bulk vapor transport through the channels. Cross-sectional TEM (transmission electron microscopy) image of the deposited film confirms that the penetration depth of DMS vapors into the 11 nm wide alumina pores is approximately 13 nm and no continuous film exists in the deeper region (Fig. 1b).

According to the AFM (atomic force microscopy) analysis (Fig. S1), surface roughness of the template is significantly reduced at the initial stage of deposition (Fig. 1c), indicating the smooth and conformal coating of the nanoporous alumina surface with the PDMS stacks. In the PVD process, the thickness of the deposited polymer film and the corresponding pore shrinkage are determined by the number of PVD cycles. Nominal lateral PDMS deposition thickness per cycle is found to be around 10 nm (Fig. 1e) on the reference non-porous flat alumina films prepared by ALD (atomic layer deposition) that chemically resembles the porous anodized alumina templates (Supplementary 3.1), based on which we estimate the lateral deposition thickness on the porous alumina supports (Fig. S2a,b). PDMS lateral coating thickness increases linearly with the number of deposition cycles and the template pore shrinks radially by the circumferential coating (Fig. 1d, inset). The pore size of the porous polymer (d_{pore}) is estimated with a proposed pore clogging model. Accordingly, the pore size declines exponentially with the deposition cycles $(d_{pore} \sim (0.55)^m d_{template}, m$ deposition cycle number, Supplementary 3.2). The effect of the pore shrinkage is clearly seen in the proportional decrease of the membrane gas permeance (Fig. S7B) and a shift in the gas selectivity after every cycle of the deposition (Fig. 2a,c). Prediction of a gas transport model with a pore size parameter matches well with the observed permeance and selectivity data; it further verifies the validity of the estimated pore size at each stage [9,17]. With more than 10 cycles of PDMS vapor deposition, the porous alumina templates are found completely covered by continuous dense films and demonstrate separation performance of the dense nanoporefree polymer film (Fig. 2a,c, 12th cycle).



Fig. 2. Single gas experimental ("ideal") selectivity of CH_4/N_2 (a) and CO_2/H_2 (c). Gas mixture ("real") selectivity for separation of 50–50% feed of CH_4/N_2 (b) and CO_2/H_2 (d) at 145 kPa and 25 °C. Dashed line corresponds to resistance model prediction with concentration polarization included. Dashed-Dot lines correspond to expected either solution-diffusion in polymer or nanochannel Graham selectivity. The trends have been replicated on three samples.

3. Results and discussion

After each cycle of PDMS deposition, we carried out single gas permeation tests with hydrogen, methane, nitrogen, and carbon dioxide. In addition, gas separation experiments were investigated in a cross-flow setup with equimolar gas mixtures of hydrogen-carbon dioxide and methane-nitrogen to trace the change in transport and separation properties with pore shrinkage and blockage. The gases are expected to transfer simultaneously through the nanochannels and the circumferential polymer coating. In all cycles, the single gas flow rate shows a linear dependence on the pressure difference following to the direct proportionality of flow rate with partial pressure difference in both nanochannel channel and rubbery polymer transports (Fig. S7A) [18,19]. The permeance decreases monotonically after each cycle upon the template pore clogging and the thickness increase of the transport path (Fig. S7B). Separation performance of a membrane can be described by permselectivity (PS) defined as the permeance ratio of two different gases in the single gas permeation tests or separation factor $(\alpha_{i/i})$ defined as the ratio of the compositions of the two gas species in a mixture in the permeates side relative to those in the feed (Supplementary 1.2). Unlike the former, the latter method considers the interactions between different gas components in a mixture and thus provides insightful information for mixed gas separation. In both cases of gas separation with methane-nitrogen and carbon dioxide-hydrogen, the permselectivity shows the Graham selectivity at low cycles of deposition, as the transport is still dominated by the nanopores than by PDMS coating (Fig. 2a,c). We note that, according to the kinetic theory of gas transport through the cylindrical channels, in the entire

transition regime between continuum or Poiseuille flow (Kn \ll 1, Kn: Knudsen number) and free molecular or Knudsen flow (Kn > 10), gas permeance scales with the inverse square root of molar mass either through the scaling of viscosity or thermal velocity with the molar mass [20,21]. Upon further deposition, the permselectivity shifts toward the property of bulk PDMS governed by the solution-diffusion mechanism [18,22]. This shift happens because at the later stages of deposition, gas transport through PDMS thin film becomes prominent, as the nanopores are gradually covered. Transition of transport mechanism from (nano) channel flow to solution-diffusion model can, therefore, be seen in the change of gas permselectivity.

Comparison between single gas and gas mixture selectivity reveals deviation of these two from each other with a possible formation of unseen minima in the transition regime between continuum and solution-diffusion transport (Fig. 2b,d). Unlike the permselectivity, the separation factor of the bare nanoporous template resides at a value close to unity, indicating apparent unselective flow near the collective regime of gas mixture transport through the bare nanoporous template (Fig. 3b), originating from the linear momentum transfer at the collision event between two gases with different molecular weights [23]. Nevertheless, upon further deposition and shrinking of the pores (1st-5th), more number of molecules travel independently, and separation factor first approaches to Knudsen selectivity of the free molecular transport (6th, Fig. 3c) and then afterwards toward bulk PDMS selectivity, which is based on the rather slow solution-diffusion transport mechanism through the free volume of polymer (Fig. 3e). In the case of methane-nitrogen separation, both free molecular transport and solution-diffusion mechanisms prefer transport of lighter gas



Fig. 3. (a) Schematic of H_2 -CO₂ gas mixture transport through pores of PDMS on porous AAO template. (b) Non-selective regime through bare template. (c) Diffusive nanochannel dominated transport through pores of porous polymer. (d) Equal contribution of diffusion transport through nanochannel pores and dense polymer. (e) Diffusion dominated transport through nanopore free polymer film.

(methane), and therefore the separation factor increases monotonically from unity toward bulk property of the polymer, and upon shrinking the pore with polymer (Fig. 2b). However, in case of carbon dioxidehydrogen separation, there is a competition between free molecular flow that prefers transport of lighter gas (hydrogen), and solution-diffusion, which in case of PDMS selects a more absorptive but heavier gas (carbon dioxide) (Fig. 2d, Fig. 3d). The competition between two mechanisms of transport leads to the formation of a minimum in the functionality of separation factor over polymer nanopore size.

We hypothesize that gas transport occurs in the parallel form through the nanopores with polymeric wall and through the polymer circumferential coating. The gas mixture separation could be affected by competitive adsorption and concentration polarization [16,24].

To validate the parallel transport hypothesis, we applied mathematical modeling with simultaneous transports through the porous and non-porous parts of the films by considering the entrance resistance into the pores, diffusion and collective flow resistances through the pores and diffusion through the dense circumferential polymer coating (1) (Fig. 4a,b; see Supplementary Information Section 4 for detail). Permeability of neither nanochannels nor rubbery PDMS remains unchanged over the entire thickness range. In the thin nanochannels, the permeability will be limited by entrance resistance [15], while in thin PDMS, it would obey diffusion along a gradient of non-equilibrium surface concentration that varies with the polymer layer thickness [14]. We assume that diffusion and collective transport occur independently and under partial pressure (ΔP_i) and total pressure (ΔP) differences respectively [25]. Realization of the model relies on the combination of the previous work of Knudsen [26], Graham [27], Sampson [28], Present [23], Unnikrishnan [15], Firpo [14], and Islam [29]. The model considers pore size distribution (F_i) at each cycle (m). Indeed, the proposed parallel transport model follows the experimental data of the single gas flow rate (N_i) (Fig. S7B), and permselectivity with a reasonable estimation (Fig. 2a,c). The model also allows us to validate the proposed dependency of the diameter of open pore with deposition cycle as indicated in the Fig. 1d inset, derived from the pore clogging model. We note that in the single gas transport study the concentration

polarization and competitive adsorption physics do not play a role.

$$N_{i,m} = \sum_{j=6nm}^{16nm} F_j \left[\frac{\Delta P_i}{R_{i,m}^{Total \ Diffusive}} + \frac{\Delta P}{R_{i,m}^{Total \ Collective}} \right]$$
(1)

Nevertheless, the parallel transport model solely cannot predict gas mixture separation performance (Fig. S8). We hypothesize that in addition to the parallel transport other transport physics are also involved in the gas mixture separation such as competitive adsorption and concentration polarization.

Comparison between the separation factor and permselectivity of uniform, defect-free thin film polymer (Fig. 2c,d, 12th cycle) reveals that single gas selectivity and gas mixture selectivity might deviate significantly for thin films depending on the target separating gases. This deviation is possibly originating from the concentration polarization (CP) at the feed side of the membrane attributable to the fast transport through the thin film. Fig. 2a,c demonstrates that at the last stages of depositions, permselectivity of both methane-nitrogen and carbon dioxide-hydrogen reaches the expected solution-diffusion values, which indicates the formation of a defect-free film. However, only separation factor of methane-nitrogen lies closely though with small deviation on the expected bulk solution-diffusion value (Fig. 2b), while in the case of carbon dioxide-hydrogen the separation factor stays below the ideal value (Fig. 2d). We hypothesize that fast transport of carbon dioxide through the carbon dioxide-selective thin film leads to the depletion of carbon dioxide concentration at the membrane surface. Previous theoretical report estimated that gas permeances as high as 100 GPU subject the membrane to gas concentration polarization [16]. Indeed, the fabricated dense film of this work with ca.1300 GPU CO₂ permeance lies above this threshold by an order of magnitude. In comparison, in case of methane-nitrogen separation, lower permeation and selectivity (CH₄: 410 GPU, CH₄/N₂: 3) than carbon dioxide-hydrogen case (CO2: 1300 GPU, CO2/H2: 4.2) inflicts the membrane on to less severe CP. To further prove our hypothesis on the CP effect, we enhanced the feeding rate to reduce CP. Indeed, increasing the feeding rate and consequent efficient mixing leads to the separation factor



Fig. 4. (a–b) Considered resistances for modeling of single gas (a) and binary gas (b) transports without concentration polarization: R_1 (effusion entrance) R_2 (Knudsen diffusion), R_3 (Sampson entrance collective), R_4 (Poiseuille collective flow), R_5 (momentum transfer), R_6 (Polymer diffusion), R_7 (Support Knudsen diffusion), R_8 (Support Poiseuille collective flow), R_9 (Support momentum transfer). Values of flow resistances vary after each cycle of PDMS deposition. (c) Effect of feed flow rate variation and pressure on the separation factor of dense PDMS membrane (cycle 12). Upstream contains 50–50% H_2/CO_2 mixture. Downstream partial pressures of H_2 , CO_2 remain constant and negligible (d) Estimated concentration of gases at the membrane surface. The values were obtained from the transport model with concentration polarization for a gas mixture separation with 50–50% feed concentration of CO_2/H_2 and CH_4/N_2 mixtures at upstream pressure of 145 kPa and 25 °C.

improvement but remained below expected material property (Fig. 4c), while increasing membrane flow by increasing inlet pressure, led to the deterioration of separation factor.

Competitive adsorption might not play profound effect on the observed deviation between the permselectivity and the separation factor. It is expected that competitive adsorption enhances the transport of adsorptive-carbon containing gases (carbon dioxide, methane) over inorganic species (hydrogen, nitrogen) [30], contrary to our observation. Furthermore, competitive adsorption on to the membrane surface is a function of applied pressure [24]. Indeed, variation of the separation factor with a change in the feed flow rate at the constant feed pressure and composition clarifies that the observed variation does not originate from the competitive adsorption of gases on the membrane surface.

It should be noted that the feeding rate of the measurements was set two orders higher than membrane flow rate at the dense state (12th cylce); however, even this rate could not provide enough mixing efficiency. These experimental results show that gas concentration polarization could reduce selectivity performance of the ultra-permeable thin polymer films.

We expanded the parallel transport model by considering a concentration boundary layer next to a flat permeable sheet (Supplementary 4.5). The thickness of the concentration boundary layer grows gradually over the length of the membrane and has dependency on the mass transfer coefficient [31]. This thickness would be negligible for the membranes with flow rates significantly lower than bulk diffusion of gases. Indeed, the expanded parallel transport model predicts the gas separation performance at different deposition cycles (Fig. 2c,d). The expanded model results in the estimated concentration of the gases at the membrane surface (Fig. 4d). These results show that the average surface concentrations deviate from the feed depending on the permeation rate of the preferred gases. In the case of carbon dioxide-hydrogen separation through the bare and partially filled nanopore, the concentration of hydrogen molecules is depleted at the interface owing to the faster transport of hydrogen. These results match with the previously observed concentration polarization near the nanopores [32] and mean that gas mixture selectivity deviates from the Graham value in the transition regime between collective and free molecular flow (1 < Kn < 10) not only because of the momentum transfer phenomenon in the channel [23] but also due to the presence of concentration polarization above the channel. However, when carbon dioxide-selective membrane forms (8th cycle), the concentration of carbon dioxide depletes near the membrane surface. Carbon dioxide concentration approaches back to the feed value upon further depositions and owing to the membrane permeance reduction. On the other hand, in the case of methane-nitrogen separation, in which the membranes remain methane selective after every stage of PDMS deposition, methane surface concentration monotonically approaches to feed value upon membrane permeance reduction.

Concentration polarization and competitive adsorption exist only in the mixture transport and their effect on the membrane selectivity might overlap. For instance, high permeable and size selective graphene oxide (GO) based membranes demonstrate the selectivity of hydrogen over carbon dioxide above 30 with hydrogen permeance lies over 1300 GPU ($400 \times 10^{-9} \text{ mol/m}^2 \text{ s Pa}$) [33,34]. In these membranes the gas mixture separation factor stays below the ideal permselectivity (i.e., 35 vs. 42 [33]) by almost 15%. This difference might be attributed to higher concentration of carbon dioxide at the membrane surface owing to the preferential adsorption on to the GO functional groups in the gas mixture transport [33,34]. From this perspective membrane intrinsic property affects the separation performance. However, considering the fast transport of hydrogen, it is expected that hydrogen concentration depletes near the surface and the intense concentration polarization deteriorates the separation factor. From this perspective dynamics of the process affects the separation performance. We note that both concentration polarization and competitive adsorption might occur simultaneously and presence of one might not influence the existence of the other one; however, they need to be distinguished for better separation process optimization.

The results presented in this communication demonstrate that fast gas transport in highly permeable, and thin polymeric membranes causes the selectivity loss owing to the CP, similar to liquid transport in the ultra-filtration membranes [35]. This understanding rationalizes further investigations on developing better mixing strategies at the feedstock of the ultrafast membranes. Configuration and geometry of the membrane play a significant role on the boundary layer growth, a subject of further investigation for optimized membrane design.

4. Conclusion

The developed process of physical vapor deposition on a porous template allowed fabrication of both porous and continuous polymer films with controlled porosity and thickness necessary for gas transport study. In the course of varying pore sizes in the polymer nanofilms, nonidentical transitions have been observed from continuum to free molecular to solution-diffusion regimes for the set of gases: methane-nitrogen and carbon dioxide-hydrogen. We developed a mathematical model that captures the transition in the transport for the ultra-thin polymeric channels of our study. It was further demonstrated that formation of gas boundary layer next to the nanopore-free, selective and highly permeable polymer film results in the apparent selectivity loss of these membranes in gas mixture transport. Concentration polarization affected selectivity of flat sheet membranes with permeance higher than 1000 GPU, tested in the cross-flow setup. Presence of concentration polarization rationalizes developing mixing strategies and optimized membrane design to benefit from an intrinsic property of high permeable membranes.

Acknowledgements

This work was carried out at Binnig and Rohrer Nanotechnology Center of ETH Zurich and IBM Zurich. A.D and M.L acknowledge Dr. Jakob Buchheim and Karl-Philipp Schlichting for their contribution to the film thickness measurement by focused ion beam microtoming. We acknowledge Dr. J.R Johnson from Saudi Basic Industries Corporation for his scientific inputs in the polymer synthesis. A part of this work was financially supported by Saudi Basic Industries Corporation exploratory research. We thank Prof. Patrick Jenny from the Institute of Fluid Dynamics at ETH Zurich for his input on the modelling of the concentration boundary layer growth.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2018.08.070.

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