Atomic-layer-deposition-enabled thin-film composite membranes of polyimide supported on nanoporous anodized alumina

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Abstract

Polyimide is deposited on the surface of nanoporous anodized alumina by atomic layer deposition (ALD) using pyromellitic dianhydride and ethylenediamine as the two precursors. Such ALD reactions directly produce polyimide rather than the intermediate polyamic acid. The precursor exposure duration plays an important role in determining the growth rate of PI and consequently the reduction of effective pore sizes. ALD with short precursor exposure confines the deposition predominantly around the pore openings of the alumina substrates, producing an asymmetric structure in the form of thin-film composites. This structure efficiently reduces the pore sizes of alumina, and as a result the retention of the membrane is significantly improved. A moderate cycle number of 50 remarkably increases the rejection of the membrane from nearly none to 82% at an acceptable expense of a reduction of 63% in water permeability. Deposition with long precursor exposure results in uniform coating into deep pores of the membranes whereas the effect in tailoring pore sizes and filtration performances are not as pronounced as deposition with short precursor exposure. This work is expected to be adopted to fabricate highly permeable and selective membranes of different materials by leveraging the deposition behavior of ALD on appropriate substrates.

1. Introduction

Polyimide (PI) is playing increasingly important roles in the field of membrane separation and has been extensively used to prepare membranes for ultrafiltration (UF) [1,2], solvent-resistant nanofiltration [3,4], gas separation [5–7] and pervaporation [8] on account of its excellent thermal, mechanical, and chemical stability [9]. The traditional way to prepare PI membranes is the phase separation process [10]. This process starts from concentrated PI solutions and the solutions are solidified in a nonsolvent to form membranes with the thickness of typically a few hundreds of micrometers. This process is flexible in tuning the microstructures of the resultant membranes and correspondingly the membrane properties. However, it consumes large amount of PI polymers as both the skin layer and the substrate layer are composed of PI. It is considered to be unfavorable because PI is much costlier than other membrane-forming polymers such as polysulfone, polyvinylidene fluoride (PVDF). Moreover, this phase inversion process is solvent extensive, and produces copious wastewater which is hard to be recycled.

To develop a more cost-efficient and environment-benign method to fabricate PI membranes, efforts have been invested in the TFC in which PI is only used to build thin selective layers on top of porous substrates. More importantly, such a composite structure allows the independent design and fabrication of the skin layers and substrate layers, thus gaining additional opportunities in tuning the membrane performances. TFC PI membranes have been prepared by a number of different methods including sol-gel process [11], vapor deposition polymerization (VDP) [12,13] and interfacial polymerization (IP) [14]. Unfortunately, these methods typically need to synthesize soluble PI precursors such as polyamic acid (PAA) [15,16] in advance. Subsequently, an imidization process is required to transform PAA to PI. Nevertheless, imidization is usually carried out in harsh conditions, for example, high temperature annealing, or solvent dehydration [17]. The imidization operations often complicate the membrane fabrication on one hand, and greatly limit the selection of substrates on the other. Therefore, it is highly desired for alternative methods for the preparation of PI membranes.

Atomic layer deposition (ALD), as a unique thin-film depositing technique with the advantages of precise thickness control and excellent uniformity [18], has recently been utilized to modify and functionalize separation membranes [19–21]. We note that the ALD deposition of polymer films like PI is also especially termed as
molecular layer deposition (MLD); however, considering that MLD exactly follows the mechanism of ALD, we remain to use the term “ALD” in this work to make it comparable to other works reporting modification and functionalization of membranes by ALD of metal oxides [19–21]. For the preparation of TFC membranes, the ALD approach is distinguished because the deposited layers can be precisely and continuously tuned simply by changing ALD cycle numbers, offering controllability and flexibility to predictably gear the properties of the composite membranes targeted to specific applications. Compared to other methods of TFC PI membranes discussed before, ALD method is an effective process directly leading to PI without the production of intermediate compound, PAA. We took the advantages of ALD to enhance the surface hydrophilicity and also to tighten the pore sizes of membranes with various structures and chemical compositions [22, 23]. Previously, we ALD-deposited PI on both polyethersulfone (PES) microfiltration (MF) and polypropylene (PP) UF membranes mainly for the purpose to enhance their surface wettability because PI is more hydrophilic than PES and PP [24, 25]. Moreover, with the deposition of PI along the membrane pores, the membranes also exhibited improved retention as a result of reduced effective pore sizes.

However, if we consider preparing composite membranes with PI selective layers, polymeric membranes are not the best choice for substrates. Firstly, polymeric membranes are typically lack of sufficiently active groups on the surface. It will result in the poor deposition quality and low growth rate of PI deposition, and it would take considerably large ALD cycles to have a uniform coverage along the pores. For example, it took about 2000 ALD cycles of PI deposition on PES membranes to observe an evident change in retention even in the case of hot plasma ALD. This is because of the low deposition quality and low growth rate of PI deposition. Therefore, it is critical to select appropriate substrate membranes to guarantee the performances of the PI composite membranes prepared by the ALD route.

To this end, we propose to use porous anodized alumina membranes as the substrates to prepare PI composite membranes. Compared to polymeric substrates, alumina membranes have an aligned, uniform pore shape [26] as well as hydrophilic surface, which is benefit for the permeability. Furthermore, the resistance ability on organic solvent allows alumina membranes to be used in harsh conditions. The extra merit of the inorganic substrates is the excellent thermal stability so that the alumina membranes can afford not only the relatively high temperature for PI deposition but also the post-treatment of PI-deposited membranes such as carbonization of PI into carbon [27]. Finally, due to the existence of active groups and narrow pore size distribution, it is more suitable to use them as substrates to investigate the influence of deposition parameters on the growth behaviors of PI and consequently the separation performances of the composite membranes.

In this work, PI is ALD-deposited on alumina membranes with a nominal pore size of 20 nm on the top surface. ALD is performed in the mode both of long exposure and short exposure, respectively. In both cases, with rising cycle numbers, the pore sizes are continuously reduced, and consequently the retention of the membrane is significantly increased at the expense of moderate loss of water permeability. Short exposure of ALD precursors is more efficient than long exposure in reducing the effective pore sizes and correspondingly improving the membrane retention because PI deposition mainly occurs around the pore openings. Thus produced TFC membranes are expected to find interesting applications in solvent-resistant separations because both PI (after crosslinking) and alumina substrates are highly stable in most organic solvents.

2. Experimental section

2.1. Materials

Chips of alumina membranes (Whatman) with a nominal pore size of 20 nm were utilized as substrates for the ALD deposition of PI. These alumina membranes are 25 mm in diameter, and they have an asymmetric structure of a skin layer (~300 nm thick) and a support layer (~60 μm thick). For each ALD treatment, alumina chips were fixed by clipping their edge using thin metal clamps to avoid being blown away by sweeping gas and positioned in the middle region in the ALD chamber. Pyromellitic dianhydride (PMDA, 99.5%, J & K Scientific) and ethylenediamine (EDA, 99.5%, Sigma-Aldrich) were used as precursors for the ALD of PI. Nitrogen with an ultrahigh purity (99.999%) was used as both the precursor carrier and the sweeping gas for purging. Bovine serum albumin (BSA) purchased from GM Corporation, with a purity of > 97% was used for rejection measurements. Purified water with a conductivity of 6 μs/cm was in-house prepared through a reverse osmosis process and used throughout this study. Dextran with various molecular weights (10, 40, 70, 500 kDa, Sigma-Aldrich) was used to determine the molecular weight cut-offs (MWCOs) of alumina membranes.

2.2. ALD of PI on alumina membranes

Alumina membranes were positioned in the chamber which was heated to 160 °C of a homemade hot-wall ALD reactor. The ALD process was commenced once the chamber was pumped to reach a vacuum of ~2 Torr. Both PMDA and EDA were stored in stainless cylinders. Considering the low volatility of PMDA with the evaporation temperature of around 150 °C [28], we maintained the storage cylinder of PMDA at 175 °C and set the deposition temperature at 160 °C so as to prevent the condensation of PMDA. EDA was much more volatile than PMDA and it was stored at room temperature. The PMDA and EDA vapor were alternatively pulsed into the ALD chamber by the carrier nitrogen gas at a flow rate of 50 sccm. The pulse duration of PMDA and EDA was 1 and 0.1 s, respectively. After pulse, PMDA and EDA were held in the chamber for 8 and 3 s, respectively, allowing the alumina membranes to be sufficiently exposed by each precursor. This condition is denoted as the mode of short exposure, and the condition is denoted as the mode of long exposure while the residence times in the chamber for PMDA and EDA are set to 20 and 10 s, respectively. Nitrogen was subsequently purged into the chamber at the flow rate of 50 sccm for 30 and 15 s after the pulse of PMDA and EDA, respectively, to sweep away the unadsorbed/unreacted precursors as well as by-products formed during the reaction between the precursors. The pulse, exposure, and purging duration for PMDA were set longer than that of EDA to allow the bulky and less volatile PMDA molecules to have adequate time to overcome the diffusion problems. Such a sequence of operations of “PMDA pulse/exposure/N₂ purge/EDA pulse/exposure/N₂ purge” is termed as one ALD cycle and all these operations are automatically controlled via fast valves. We repeated the ALD cycle for different times up to 300. PI is also deposited on the smooth surface of silicon wafers under the condition identical to the deposition on alumina substrates.

2.3. Characterizations

Surface morphology of the PI-deposited alumina membranes was performed on a Hitachi S4800 Field Emission Scanning Electron Microscopy (FESEM) operated at the voltage of 5 kV and the current of 10 μA. A thin layer of Pt/Pd alloy sputtering was pre-coated on the samples to avoid surface charging. The pore-size distribution and the
mean pore size of alumina membranes subjected to different ALD cycles were analyzed based on at least 100 pores randomly picked up from the SEM images using an image analysis program (NanoMeasure). The Fourier transformation infrared (FTIR) spectra of samples were obtained from a Nicolet 8700 FTIR spectrometer in the transmission mode. A spectroscopic ellipsometer (Compete EASEM-2000 U, J. A. Woollam) with the wavelength ranged from 246.1 to 999.8 nm in an incident angle of 70° was applied to measure the thickness of the PI films deposited on the surface of Si wafers. The initial SiO₂ layer was determined with a thickness of 2.5 nm and then subtracted. More than 5 spots on the surface of Si wafer were selected and the average value was reported for the thickness.

2.4. Evaluation of the filtration performance

Water permeability and retention rate of the pristine and PI-deposited alumina membranes were performed using a dead end, stirred filtration cell (Amicon 8003, Millipore Co., Billerica, MA). The feed side was connected to a high-pressure nitrogen tank to keep the feed pressure at 1 bar. A magnetic stir bar was used to stir the feeding solution at a spinning rate of 600 rpm to minimize concentration polarization. To test the protein retention, the proteins were dissolved in phosphate buffers (pH = 7.4) at a concentration of 0.5 g/L. The concentrations of BSA in the permeate side were obtained using a Nano DROP 2000C UV–vis spectrophotometer at a wavelength of 280 nm. The retention for dextrans was studied by the filtration of dextran solutions with concentration of 6.5 g/L. The dextran solutions were analyzed by gel permeation chromatography (GPC). GPC of dextran was performed with Ultrahydrogel columns using a Waters Isocratic HLPC 1515 pump and a Waters 2414 refractive index detector. The molecular weight of the dextran corresponding to a 90% retention level was taken as the MWCO of the membrane. The concentration of dextran in the feed and permeate solution, respectively. The retention rates (R) of both BSA and dextran can be calculated through the following equation:

\[ R(\%) = (1 - C_p/C_f) \times 100 \]  

where R is the retention rate of the membrane, \( C_f \) and \( C_p \) is the concentration in the feed and permeate solution, respectively.

3. Results and discussion

3.1. Determination of the chemical composition of the deposited layers

We first deposited both a piece of alumina membrane and silicon wafer for 300 cycles in the mode of short exposure and examined their appearance. After deposition the alumina membranes maintains its original white color; however, the color of silicon wafer, which was placed aside by the alumina membranes in the reaction chamber, turns blue. This color change demonstrates the existence of new substance on the surface. Since the reaction between PMDA and EDA can also produce the intermediate compound, PAA [29], in addition to the final product, PI, it is necessary to identify the composition of the deposited layers. To this end we used FT-IR to analyze the produced material on the silicon surface. As shown in Fig. 1, three new peaks appear and become stronger with increasing cycle numbers, which suggests that higher ALD cycles lead to thicker deposited layers. The three new peaks at the wavelength of 1389, 1714, and 1773 cm⁻¹ represent the stretching vibration of C-N bonds, the symmetrical and asymmetrical stretching vibration of C=O bonds, respectively [30], which are all originated from PI. Nevertheless, no characteristic peak of PAA at 1640 cm⁻¹ can be observed in the spectra no matter how thick the deposited layer is. Furthermore, the IR spectra imply that there is no any residual monomer on the silicon wafers as no characteristic peak of amine (3300–3500 cm⁻¹) [31] or anhydride (1806 and 1860 cm⁻¹) can be detected. The material formed on the silicon wafer should be the same with that formed on the alumina membranes although the growth rate might be different as we will discuss later. Therefore, we conclude that through such an ALD process we directly obtained PI rather than PAA, and therefore, imidization which is typically required in the synthesis of PI by different methods, is no longer necessary.

3.2. Determination of the growth rate of PI

The ALD process of PI on alumina membranes is composed of the following sequence: PMDA dose, expose, \( N_2 \) purge, EDA dose, expose, \( N_2 \) purge. These four steps form a full cycle of PI ALD and deposited PI layers with a specific thickness can be obtained. For the sake of analyzing the growth mode of PI on alumina membranes, we first tried to measure the weight gain of alumina membranes with different cycle numbers. However, due to the ultrathin feature of PI layers, the change of weight is too slight to be detected by the analytical balance. Therefore, an indirect method was utilized by monitoring the change in the thickness of PI layers on silicon wafers, instead of alumina membranes, with respect to various ALD cycles because the thickness of the deposited layers can be precisely measured by ellipsometry. As revealed in Fig. 2, there is a linear increase in the thickness of PI layers with rising ALD cycle numbers. For instance, the thickness of the deposited layer is 12 and 18 nm with 30 and 50 cycles deposition, respectively. Moreover, the thickness reaches 36 nm after 110 cycles of PI ALD. Consequently, we can determine that the growth rate is

![Fig. 1. The FTIR spectra of the ALD-deposited layers on silicon wafers with different cycle numbers.](image)

![Fig. 2. Thicknesses of PI layers prepared with various ALD cycle numbers in the mode of long and short exposure time, respectively.](image)
0.32 nm per cycle under these deposition conditions, which is close to previously reported value for the ALD deposition of PI [28]. These ellipsometric characterizations were also performed on the silicon wafers deposited in the mode of long exposure to investigate the effect of exposure time of precursors on the growth rate. As shown in Fig. 2, there is no remarkable difference in the growth rate between these two deposition modes possibly because of the flat and nonporous surface of silicon wafers.

### 3.3. Morphology evolution of alumina membranes with PI deposition

Surface morphologies of alumina membranes before and after PI deposition were characterized by SEM. Alumina membranes fabricated by a two-step anodization process [32] possess a honeycomb structure with a relatively high porosity, as shown in Fig. 3a. We first discuss the morphology evolution of alumina membranes deposited in the mode of short exposure. With the increment of ALD cycles, the skeleton of alumina membranes became increasingly thick due to the PI coating deposited on the surface as well as on the pore wall of alumina membranes. In comparison with the neat alumina membranes, the surface of alumina with PI deposition became smoother which can attribute to the conformal feature of ALD. In addition, the effective pore sizes of alumina membranes drop continuously with the increase of deposition cycles (Fig. 3b–e). After 110 cycles of ALD, a defect-free and dense PI coating was formed on the alumina membranes (Fig. 3f). In contrast, small pores are still present on the surface of the alumina membrane prepared with 110 cycles in the mode of long exposure (Fig. 3g), which is similar to the membrane prepared with 90 cycles in the short exposure time (Fig. 3e). Such observations imply that the growth rate in the mode of short exposure is faster than the mode of long exposure. In order to figure out the reason behind, we examine the cross-sectional morphologies of 110-cycle-deposited membranes prepared in both modes (Fig. 3h, i). It is clear that the PI growth gives priority to the surface and pore openings for deposition in the mode of short exposure time whereas PI tends to grow along the pore wall and penetrate into deep interior of the pores in the mode of long exposure because of sufficient diffusion of precursors [33].

### 3.4. Growth mode of PI with short and long precursor exposure

To further investigate the change in the pore size with cycle numbers, we analyzed the distribution of pore size (insets in Fig. 3a–g) and estimated the mean pore size of each membrane sample. Fig. 4 indicates the change of the mean pore size of alumina membranes subjected to different cycle numbers in the mode of long and short exposure. A nearly linear relationship between the mean pore sizes and ALD cycle numbers can be observed in both cases. For instance, the mean pore size of the bare alumina membranes is 32 nm, and it drops to 24, 19, 16 and 10 nm after 30, 50, 70 and 90 cycles of PI ALD in the mode of short exposure, respectively. The reduction rate of the mean
The mean pore size of alumina membranes is approximately 0.24 nm per cycle in the mode of long exposure. In the short exposure mode, the growth rate is ~0.16 nm per cycle. The adsorption/desorption process of precursors during exposure time, once the exposure time is prolonged, precursors penetrate into deep inside. Since there is an adsorption/desorption process of precursors during the exposure time, the growth rate of the mean pore size is ~0.24 nm per cycle.

Compared to the growth rate of PI at silicon wafers (0.32 nm per cycle), the growth rates at alumina membranes (half of the reduction rate of the mean pore size, 0.12 nm and 0.08 nm for the deposition of short and long exposure, respectively) are considerably low. The possible reason is that the silicon wafer is flat so there is no need for PI to penetrate into porous structure. However, the growth rates on alumina membranes are about 4-6 times larger than that on PES membranes (~0.019 nm per cycle) because the surface of alumina covered by hydroxyl groups provides more active sites for the adsorption and reaction of ALD precursors. Moreover, compared to our previous works depositing metal oxides on polymeric or ceramic membranes [20,21], the growth rate of PI ALD is also much higher, which is very desirable because it makes the tuning of pore sizes more time- and cost-efficient.

The change of the mean pore size of alumina membranes with cycle numbers in the mode of long and short exposure.

The permeability of PI-deposited alumina membranes with short exposure time. The neat alumina membranes presented a water permeability of 2226 Lm⁻²h⁻¹bar⁻¹ and a BSA retention as low as 1.6%. After PI deposition, the water permeability declines to 821 Lm⁻²h⁻¹bar⁻¹ for 50 cycles and further declines to 131 LmHbar⁻¹ for 90 cycles. At the same time, the BSA retention of alumina membranes is enhanced significantly with increasing cycle numbers. For instance, the BSA retention of alumina membranes is increased to 82% and 91% after 50 and 90 cycles of PI ALD, respectively. When the cycle number reaches 110, the water permeability was neglectable under the feed pressure of 1 bar. The increase in retention and the decrease in permeability of the deposited alumina membranes well correspond to the changes of pore sizes as revealed by SEM imaging (Fig. 3).

Water permeability and BSA retention of PI-deposited alumina membranes prepared by different cycle numbers in the mode of both long and short exposure are shown in Fig. 6. Generally, the results exhibit the trade-off effect on permeability and BSA retention. The permeability drops and retention rises due to the narrowed mean pore sizes with increasing ALD cycles. We first investigate the filtration performances of the PI-deposited alumina membranes with short exposure time. The neat alumina membranes presented a water permeability of 2226 LmHbar⁻¹ and a BSA retention as low as 1.6%. After PI deposition, the water permeability declines to 821 LmHbar⁻¹ for 50 cycles and further declines to 131 LmHbar⁻¹ for 90 cycles. At the same time, the BSA retention of alumina membranes is enhanced significantly with increasing cycle numbers. For instance, the BSA retention of alumina membranes is increased to 82% and 91% after 50 and 90 cycles of PI ALD, respectively. When the cycle number reaches 110, the water permeability was negligible under the feed pressure of 1 bar. The increase in retention and the decrease in permeability of the deposited alumina membranes well correspond to the changes of pore sizes as revealed by SEM imaging (Fig. 3). We note that the reduced permeability after PI deposition is well compensated by the significantly increased rejection. For instance, after deposition with 50 cycles, the alumina membrane experienced a 63% reduction of permeability; however, it is compensated by more than 50 folds of increase in rejection. Moreover, moderate ALD cycles, e. g. 50, are able to drastically change the separation performances of alumina membranes. This should be attributed to the fast growth of PI on the surface of alumina membranes. In contrast, in the case of using polymeric membranes as substrates, it needs several hundreds or even thousands of ALD cycles to noticeably change the filtration properties of the membranes [24,25].

We then measured the filtration properties of the membranes deposited in the mode of long exposure to investigate the effect of exposure time on the membrane performances. As shown in Fig. 6, the trend of permeability and BSA retention change with ALD cycle numbers is similar to those of membranes deposited in the mode of short exposure. The main difference is that membranes prepared in the mode of long exposure always exhibit higher permeability and lower BSA retention than membranes deposited in the mode of short exposure with the same ALD cycle number. For instance, the membrane subjected to 50 cycles in the mode of long exposure gives a permeability of 1370 LmHbar⁻¹ and a BSA rejection of 18%, whereas these values are 821 LmHbar⁻¹ and 82%, respectively for the membranes deposited in the mode of short exposure for 50 cycles. Clearly, the exposure time of precursors significantly influences the filtration properties, and short
exposure is more efficient in narrowing down the surface pores because in this mode PI deposition is predominantly occurs around the pore openings, thus producing an asymmetric structure on top of the alumina substrates. Therefore, if considering only tuning the pore size to increase the rejection one should adopt short exposure of precursors. From the practical point of view, short exposure consumes less precursors and operation durations, which is also highly desired. In contrast, long exposure is necessary to produce a uniform coating along the deep pores for the purpose of, for example, template synthesis of one-dimensional nanomaterials [34,35].

To further identify the separation performance of PI-deposited alumina membranes, we selected the 90-cycle-deposited membranes with short exposure time which exhibits a high BSA rejection (91%) and a moderate water permeability (131 LMHbar⁻¹) for the test of dextran retention. In this test, a mixed solution of dextran with four different molecular weights (500, 70, 40, 10 kDa in sequence) in the feed and filtrate solution were obtained. The dextran with the molecular weight of 500 kDa are completely rejected as the peak of corresponding responsive values obtained. The dextran with the molecular weight of 40 and 70 kDa are partly rejected. The dextran-retention curve with 90 cycles of PI ALD was presented in Fig. 8 and we can determine that the MWCO of this membrane is 41 kDa.

4. Conclusion

In this work, thin-film-composite membranes are prepared by ALD deposition of PI on nanoporous anodized alumina. When ALD precursors are exposed to the alumina substrates for short durations deposition mainly takes place around the pore opening, thus producing an asymmetric structure with the deposited PI as the top layer. Such a composite structure favors tight retention at a moderate expense of permeability. A low cycle number of 50 leads to the remarkable upgrade of retention from nearly none for the neat alumina substrate to 82% while the water permeability still maintains as high as over 800 LMHbar⁻¹. Moreover, long exposure of precursors is also exploited in the ALD process to investigate the differences of PI growth mode. Long exposure allows precursors penetrate deeply into deep interiors of the pores in alumina membranes, producing uniform thin deposition along the pores. It also shows the effect of tailoring pore sizes and consequently increasing the retention capability, but its effect is less pronounced compared to short exposure. Considering that a large number of polymers, metal oxides, and metals can be deposited on many different porous substrates we expect this strategy to be widely adopted to design and fabricate highly permeable and selective thin-film-composite membranes by carefully balancing the growth behavior of the materials to be deposited and the porous nature of the substrates.

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