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Rapid Assembly of Polyelectrolyte Multilayer Membranes Using an Automatic Spray System

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The layer-by-layer (LbL) assembly of polyelectrolyte multilayers on to a porous supporting membrane is able to create various new composite membranes. However, the low efficiency and long time required for such procedures limit practical applications. In this study, an automatic spray system has been constructed for the rapid assembly of polyelectrolyte multilayers on to nanoporous supporting membranes. The compounds polyacrylic acid and poly(ethyleneimine), used as a model polyelectrolyte pair, were alternately sprayed on to a polyacrylonitrile ultrafiltration membrane. Experiments proved that the composite membrane obtained in this way had a good pervaporation dehydration performance. In addition, the process times were dramatically decreased, by as much as 80 folds, when compared with classical dip-LbL methods. Such an automated system can easily be converted to the assembly of various organic species. Therefore, it is a versatile and highly efficient system for manufacturing composite multilayer membranes for many separation applications. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 250–257, 2013

Keywords: spray layer-by-layer (spray-LbL), technique, polyelectrolyte multilayer membranes, pervaporation

Introduction

In recent years, molecular self-assembly techniques have been widely used to create uniform films with nanometer control. In particular, the layer-by-layer (LbL) assembly technique, consisting of alternating deposition of oppositely charged polymers on to porous supports, has proven to be a versatile tool for the creation of new dense composite membranes.[1,2] For example, it has been demonstrated that LbL-assembled composite membranes can serve a wide range of uses such as pervaporation,[3–6] gas separation,[7–9] nanofiltration,[10–12] reverse osmosis,[13–15] and forward osmosis.[16,17] For such dense composite membranes, the mass transport across the membranes is governed by a solution–diffusion mechanism. Therefore, the key feature is that the ultrathin selective layer on the porous supports must be defect-free. Obviously, LbL assembly has an advantage for the preparation of such defect-free layers because each added layer is used to cover the defects in previous layers. Typically, the LbL deposition process involves the submersion of a charged substrate alternately in contact with a polyanion or a polycation solution, each followed by a rinse step to eliminate the excess polyelectrolytes on the surface. Although, this conventional deposition process by dipping is in widespread use and easy to do, it is also a redundant and a cumbersome procedure.[6,18] Usually, it requires dozens of hours or even several days to prepare a membrane with adequate properties. Therefore, it is necessary to look for a more rapid and simpler process if this technology is to extend into industrial applications. In fact, our group has been committed to the simplification of the LbL procedure for a long time. For example, we utilized a dynamic LbL process to prepare polyelectrolyte multilayers on both flat-sheet and hollow fiber UF membranes, which significantly reduced the deposition cycles while retaining good pervaporation properties.[19–23] Lee and coworkers have developed the LbL assembly of a poly(((4,4’-bis(6-dimethylammonio)hexyl)-oxy)azobenzene bromide) (PAZ-6) and carrageenan multilayer by using a spin-coating method.[24] They demonstrated that the spin method could strikingly reduce the preparation time per single layer to about 20 s and, at the same time, the surface was much smoother than those prepared by the dipping method.[25,26] More recently, Fu and Li have reported the use of an agitated-dipping LbL technique to fabricate poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonic acid) sodium salt (PSS) multilayer films on quartz slides, which reduced the dipping time to a few tens of seconds. It has been demonstrated that with the assistance of vigorous agitation, the assembly efficiency is greatly promoted, thus diminishing the deposition time.[27] Even though many approaches have been proposed to build up LbL films more rapidly, the preparations of selective separation membranes have not yet been studied.[28,29] Moreover, most of the previous studies have used a manual and batch operation, which inevitably introduces some variations due to human factors.

In 2000, a relatively new procedure, first introduced by Schlenoff’s group and known as spray-LbL was used to create multilayers in much shorter times.[30] By sequential spraying of polyanion and polycation solutions on to a vertical charged surface, a film of equivalent quality, composition,

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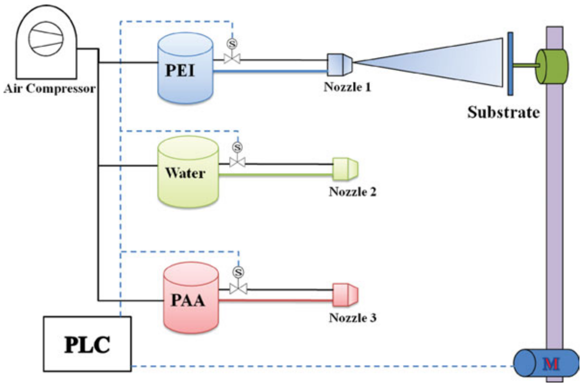

Scheme 1. Automatic spray system for the preparation of flat sheet polyelectrolyte multilayer membranes.

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and morphology to those prepared by the dipping method can be obtained. For instance, Decher and coworkers have reported the fabrication of multilayers by successive spraying of poly(styrenesulfonate) (PSS) and PAH solutions on to a PEI precursor layer. Each bilayer can be constructed in about 2 min as compared to about 50 min via the classical dipping method.[31] Krogman et al. have described an automated system to prepare polyelectrolyte multilayers (PEMs) using a film growth technique similar to the dipping LbL assembly method. They demonstrated the utility of traditional polyelectrolytes for the assembly of PEMs and applied the technique to a hydrogen-bonded system, dendritic compounds and colloidal nanoparticles.[32] Both the spray pressure and the mass transfer of the polyelectrolyte from the bulk solution to the substrate surface may play an important role in decreasing the process time. In addition, Schaaf and Porcel have further developed the spray-LbL technique to give a so called simultaneous spray coating of interacting species (SSCIS) process, leading to the formation of numbers of systems including those on polyanion/polycation films like the PGA/PAH system (poly(glutamic acid) (PGA) and poly(allylamine) (PAH)). The interaction between polyelectrolytes with some small, oppositely multicharged molecules, such as PAH/citrate mingled with glutaraldehyde (GA), leads to the formation of a covalent network. While in inorganic environment, the interaction between complementary inorganic ions, such as aqueous solutions of calcium chloride and sodium fluoride, leads to the formations of a dense layer of CaF_2.[33–35] Despite the increasing development of spray-LbL assembly process, most previous studies have focused on the control of film growth, thickness, and morphology. However, the spray-LbL assembly of multilayer membranes for separation applications still remains largely unexplored.

In this work, an automatic spray-LbL apparatus has been developed to construct a defect-free ultrathin selective layer on a porous support membrane. To prove the feasibility of preparation of a separation membrane using the spray-LbL assembly process, poly(ethyleneimine)/poly(acrylic acid) (PEI/PAA) was selected as a model polyelectrolyte pair to fabricate multilayer membranes. The aqueous polycation and polyanion solutions were, in turn, sprayed horizontally on to the vertical PAN substrate, followed by a spray of ultrapure water to rinse off the excess polyelectrolyte each time. Different from SSCIS process, the substrate automatically moved to the preset location for the subsequent assembly after each spraying step. The stepwise growth of the polyelectrolyte multilayer was tracked through the variations of the surface zeta potentials during the spraying process. Micrographs of the spray assembled membranes were observed by using a scanning electron microscope (SEM) and an atomic force microscope (AFM). Finally, the pervaporation separation behavior for alcohol/water mixtures was investigated following different assembly conditions.

Experimental

Materials

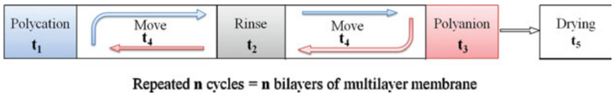
Branched poly(ethyleneimine)(PEI), with a molecular weight of 60,000, was purchased from Acros. The polyacrylic acid (PAA) powder, having an average molecular weight of 4,000,000, was obtained from Aldrich. All the aqueous polymer solutions were used without pH adjustment and the addition of ionic salt in the spray assembly process. Sodium hydroxide, ethanol, isopropanol, isobutanol, and ethyl acetate were obtained from Beijing Chemical Factory. All chemicals were of analytical grade and used without further purification. Flat sheet PAN ultrafiltration (UF) membranes with a nominal molecular weight cutoff of 30,000–40,000 were supplied by Sepro Membranes.

Automated spray-LbL apparatus

The automated spray system was constructed in our laboratory and is represented schematically in Scheme 1. The equipment consists of three identical atomizing nozzles with a nozzle diameter of 0.5 mm, each connected to a pressure tank and a solenoid valve that controls the opening and closing of the nozzles. A high volume air compressor was utilized to maintain a constant pressure of 3 bar inside the three pressure tanks while spraying. During both spraying and washing processes, a rubber substrate was fixed perpendicularly and rotated at 6 rpm solely to accelerate the drainage of the solution and rinsing water from the surface of the films. All operations, such as the time of spraying and draining, rinsing time, and the number of repetitions, were controlled by a programmable logic controller (PLC) system as variable parameters.

Preparation of polyelectrolyte multilayer membrane using spray-LbL assembly

For the preparation of a defect-free pervaporation composite membrane, PEI/PAA pairs were assembled on to the flat porous sheet of hydrolyzed PAN substrate. Following our previous study, the PAN UF membrane was hydrolyzed for 30 min at 65°C by immersing it in 2 N NaOH aqueous



Scheme 2. Schematic illustration of the spray-LbL assembly of multilayer membranes.

(t_1, t_2, and t_3 are the process time of assembling polycation, ultrapure water, and polyanion, respectively. t_4 represents the required interval between two deposition cycles, t_5 is the drying time for the final treatment. n is the number of bilayers.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solution to obtain a negatively charged surface.[19] The hydrolyzed membrane was cut into 10 cm squares which were then fixed perpendicularly on to the rubber substrate. Both polyelectrolyte solutions and rinse water were used at their default pH without adding salt and adjusted to a flow rate of 1.8 ± 1.5 mL/s when spraying. The distance between the substrate and spray nozzles was fixed at 45.0 cm, and the sprayed area was a circle of diameter more than 10.0 cm. The spray process was performed as shown in Scheme 2. As shown in Scheme 2, unless indicated, the LbL sample were prepared at $t_1 = 3\text{s}$, $t_2 = 3\text{s}$, $t_3 = 3\text{s}$, $t_4 = 27\text{s}$, $t_5 = 30$ min. To remove the remaining water, the multilayer samples were placed in a convection oven set at 50°C for 30 mins.

Pervaporation experiments

The procedure and the measurement apparatus used in the pervaporation experiments have been described in our previous studies.[20] The effective area of the membrane in the permeation equipment was 24.6 cm^2. The feed aqueous solution had a ethanol concentration of 95.0 wt %, while the feed temperature was 65°C. The down-stream pressure was about 200 Pa and monitored by a digital vacuum gauge. The permeate vapor was trapped with liquid nitrogen and measured by gas chromatography (GC-14C, SHIMADZU) with the thermal conductivity detector. Three parallel multilayer membranes were assembled in the exactly same way. Each membrane obtained was measured three times under the same pervaporation conditions. Fluxes were determined by measuring the weight of liquid collected in the cold traps over a certain time under steady-state conditions. The permeation flux (J) and separation factor α stand for the permeability and selectivity, respectively. The separation factor (α) was calculated according to the following equation, with Y_w and X_w representing the weight fraction of water in the permeate and feed.

$$\alpha = \frac{Y_w(1 - X_w)}{X_w(1 - Y_w)}$$

Characterization

The zeta potentials were determined using an electrokinetic analyzer (SurPASS, Anton Paar). The top surfaces and cross-sections of the PEI/PAA complex membranes were observed with a scanning electron microscope (SEM) (Hitachi S-4300, Japan). The membrane samples were fractured in liquid nitrogen and gold-coated before observation. Surface topography was also performed in tapping mode using an atomic force microscope (AFM) (Pico Scan^{TM} 2500). All the samples for SEM and AFM characterizations were air dried.

Results and Discussion

The step-by-step buildup of polyelectrolyte multilayers using electrostatic forces is usually performed by the alternating adsorption of two types of oppositely charged polymeric chains. Charge overcompensation of the interacting groups after each deposition step allows the buildup process to proceed. Therefore, it is very important to understand the variations of substrate surface charge properties after alternately spraying polycation and polyanion solutions. Measurement of the zeta potential has been demonstrated to be a useful approach to monitor the stepwise growth of sequential polymer layers during the LbL assembly process.[22,36,37] The surface zeta potential was tracked using an electrokinetic analyzer before and after spraying polyelectrolyte layer on to the flat sheet porous polymeric substrate. The surface zeta potential as a function of the number of PEI/PAA layers is shown in Figure 1. It was noted that the alkaline hydrolyzed PAN surface had a negative value of −60.1 mV due to the formation of the negatively charged carboxylate groups. The charge of the supporting surface could be reversed, becoming positively charged after spraying with one PEI layer. The zeta potential then changes between −10.0 and +10.0 mV when PAA and PEI, respectively, were alternately sprayed on to the surface. These regular changes of the zeta potential indicated the successful stepwise growth of PEI/PAA layers on the surfaces of the hydrolyzed flat sheet PAN substrates.

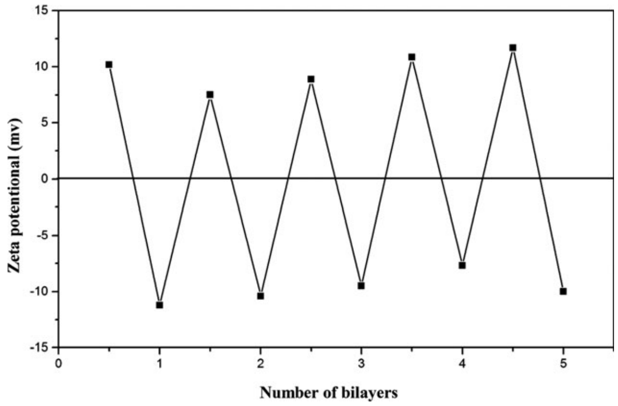


Figure 1. Variations of top surface zeta potential with layer numbers (Hydrolysis conditions for PAN support membrane: temperature 65°C, time 30 min.

Preparative conditions for spray-LbL assembly: $t_1 = 3\text{s}$, $t_2 = 3\text{s}$, $t_3 = 3\text{s}$, $t_4 = 27\text{s}$, and $t_5 = 30$ min; 0.125 wt % PEI aqueous solution, 0.025 wt % PAA aqueous solutions; 25°C.)

To clearly observe the changes of the surface morphology,the multilayer membranes obtained from the spray LbL technique were examined by SEM with the results shown in Figure 2. We clearly observed that, at low image magnification (100 times), the sprayed multilayer surface has many spherical or worm-like bumps with different sizes, which increased progressively with the number of sprayed bilayers. It is well recognized that polyelectrolyte adsorption is a two step process: polymer chains are anchored to the substrate surface during a fast initial step, and then relax to dense packing during a slower second step. Usually, the second step may take much time. The surface rearrangement of the adsorbed chains was completed in the second step. Particularly, in case that the adsorption time is long enough, the PE chain will be sufficiently stretched. During the spray-LbL assembly, cycle times for the generation of LbL films using spray-LbL are of the order of tens of seconds. This meant the polycation/polyanion did not have enough time to fully stretch. Therefore, that the interaction between polycation and polyanion was proceeded in the states of coiled or aggregated form. This may lead to the formation of bumps. As shown in Figure 2a-1, many nanoscale pores were observed (with a magnification of ×100,000) on the surface of the hydrolyzed PAN membrane before spraying. For comparison, a nonporous and dense layer was obtained with 30 PEI/PAA bilayers (Figure 2b-1).

To characterize the morphology changes better, an inspection of the top surface by AFM after spraying polycation and polyanion is revealed in Figure 3. The values of mean roughness (Ra) were obtained based on a 20.0 μm × 20.0 μm scan

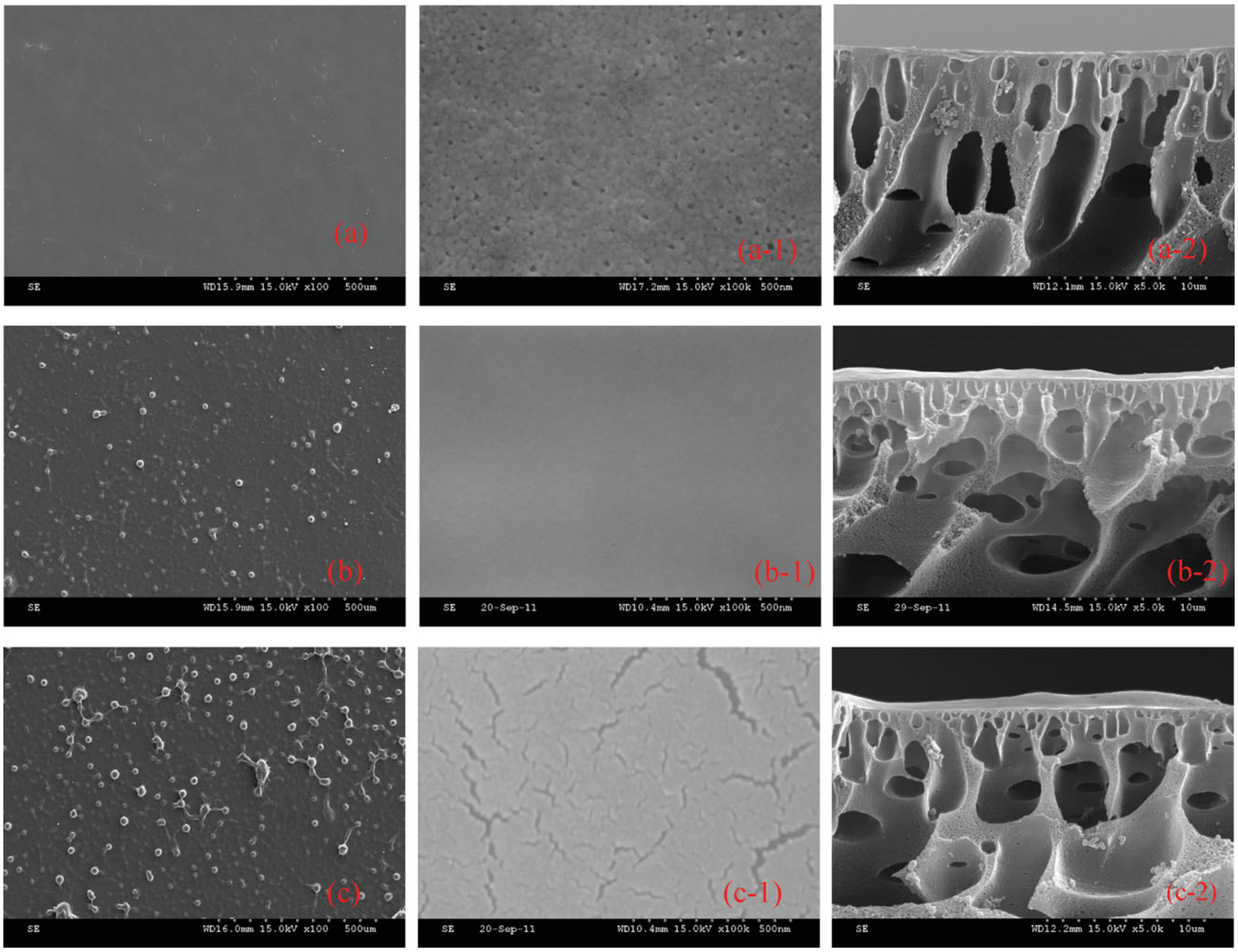


Figure 2. SEM images of the flat sheet multilayer membranes assembled by spray-LbL technique.

(a) Surface image of PAN membrane before spraying assembly (100.0×). (a-1) Surface image of PAN membrane before spraying assembly (100.0k×). (a-2) Cross-sectional image of PAN membrane before spraying assembly (5.0k×). (b) Surface image of multilayer membrane sprayed with 30 bilayers of PEI/PAA (100.0×). (b-1) Surface image of multilayer membrane sprayed with 30 bilayers of PEI/PAA (100.0k×). (b-2) Cross-sectional image of multilayer membrane sprayed with 30 bilayers of PEI/PAA (5.0k×). (c) Surface image of multilayer membrane sprayed with 50 bilayers of PEI/PAA (100.0×). (c-1) Surface image of multilayer membrane sprayed with 50 bilayers of PEI/PAA (100.0k×). (c-2) Cross-sectional image of multilayer membrane sprayed with 50 bilayers of PEI/PAA (5.0k×). (Preparative conditions for spray-LbL assembly: t_1 = 3s, t_2 = 3s, t_3 = 3s, t_4 = 27s, and t_5 = 30 min; 0.125 wt % PEI aqueous solution,0.025 wt % PAA aqueous solutions; 25°C.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

area. Figure 3a shows the three-dimensional AFM image of the hydrolyzed PAN membrane before assembly for which the Ra value was 156 nm. It was noted that the top surfaces became much rougher after alternately spraying PEI and PAA solutions as the PEI/PAA pairs were successfully assembled on to the membrane surface due to the electrostatic adsorption (Figures 3b, c). For example, the Ra of the PEI/PAA multilayer membranes increased from 211 to 236 nm with 15 and 30 bilayers, respectively. The increase of membrane surface roughness might be attributed to the aggregation of polyelectrolytes after the polymer chains had been kinetically assembled at the point of contact with the substrate.

With regard to the LbL-assembled multilayer membranes, the separation capability can be precisely controlled by varying the number of bilayers. The pervaporation performances with different numbers of PAA/PEI layers are shown in Figure 4. It was noted that the trend of pervaporation efficiency can be divided into three stages with respect to increasing numbers of sprayed PEI/PAA bilayers. From 5 to 20 bilayers, the separation factor exhibited a linear increase while the flux decreased linearly. For example, the water content of the permeate was 55.3 wt % and the flux was 612 g/h m^2 for a 5 bilayer membrane. When the number of PEI/PAA bilayers was increased to 20, the water in the permeate increased to 95.7 wt % while the flux decreased to 264 g/h m^2. Clearly, the separating layer became denser and more compact with increasing numbers of spray cycles of the polyelectrolyte pairs. As the number of bilayers increased from 20 to 30, both flux and water in the permeate slowly changed. After more than 30 bilayers, the trend of pervaporation properties as a function of the number of PEI/PAA bilayers reached a more or less steady-state. The multilayer membrane with 30 PEI/PAA bilayers had a separation factor of over 2000 and a flux of about 180 g/h m^2. The selectivity was higher than those from 30- and 60-bilayer assemblies using traditional dip-LbL.[3,18] It appears that once a defect-free selective layer is achieved, higher numbers of bilayers have insignificant effects on the separation efficiency. On one hand, the increase in the LbL bilayer number lead to the film thickness increase, which has the tendency to decrease the membrane flux. On the other hand, when the bilayer number increased, the water swelling of upper layer increased since the binding force between the upper layers with supporting membranes weakened, which is beneficial for the flux increase. Therefore, there should generally be a compromise between pervaporation efficiency and bilayer number because higher number membranes are usually much more easily swelling.

It has been shown that the spray of pure water served to rinse off the excess polymer on the surface and is therefore directly bound up with the film quality and structure.[23] Therefore, the effects of rinse time on the pervaporation performance were also studied. As shown in Figure 5, in the case of both 20- and 30-bilayer assemblies, a relatively good

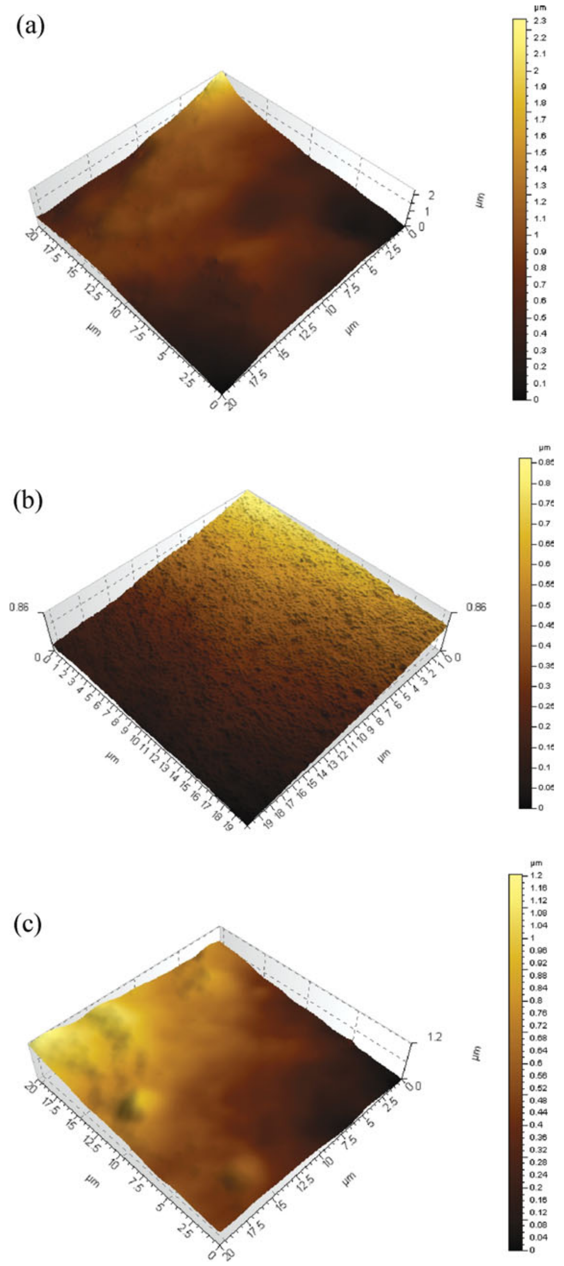


Figure 3. Tapping mode 3-D AFM images of multilayer membranes (20.0 μm × 20.0 μm) (a) PAN support membrane before assembly (Ra = 156 nm) (b)multilayer membrane with 15 bilayers of PEI/PAA (Ra = 211 nm) (c) multilayer membrane with 30 bilayers of PEI/PAA (Ra = 236 nm) (Hydrolysis conditions for PAN support membrane: temperature: 65°C, time 30 min. Preparative conditions for spray-LbL assembly: t_1 = 3s, t_2 = 3s, t_3 = 3s, t_4 = 27s, and t_5 = 30 min; 0.125 wt % PEI aqueous solution, 0.025 wt % PAA aqueous solutions; 25°C.)

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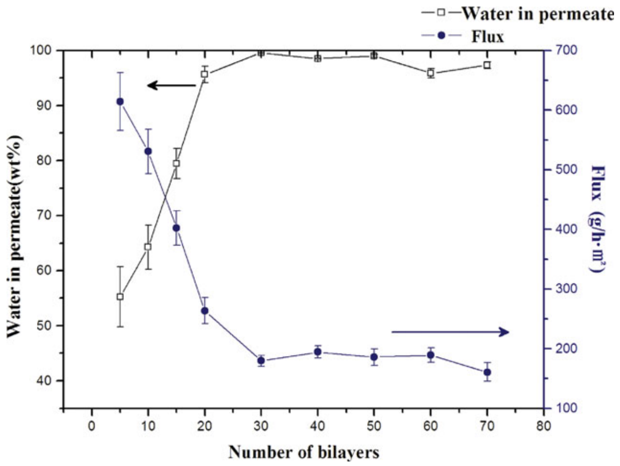

Figure 4. Correlation of flux and water in permeate to layer pair number for the (PEI/PAA)$_n$ system.

(Preparative conditions for spray-LbL assembly: t_1 = 3s, t_2 = 3s, t_3 = 3s, and t_4 = 27s; 0.125 wt % PEI aqueous solution, 0.025 wt % PAA aqueous solutions; 25°C. Pervaporation conditions: feed solution temperature 65°C, down-stream pressure 200 Pa, water content in feed solution 5.0 wt %).[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

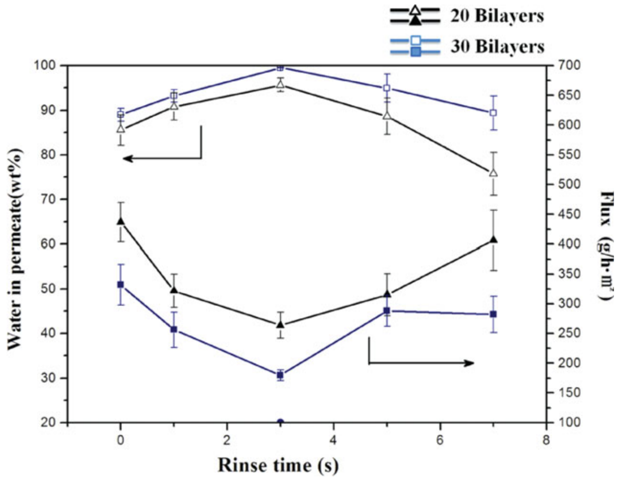

Figure 5. Effects of rinse time on the pervaporation performances of 20- and 30- bilayer membranes.

(Solid triangle(▲) and square (■) correspond to the flux, and hollow triangle(△) and square(□) represent the water content in permeate. Preparative conditions for spray-LbL assembly: t_1 = 3s, t_3 = 3s, t_4 = 27s, and t_5 = 30 min; 0.125 wt % PEI aqueous solution, 0.025 wt % PAA aqueous solutions; 25°C. Pervaporation conditions: feed solution temperature 65°C, down-stream pressure 200 Pa, water content in feed solution 5.0 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

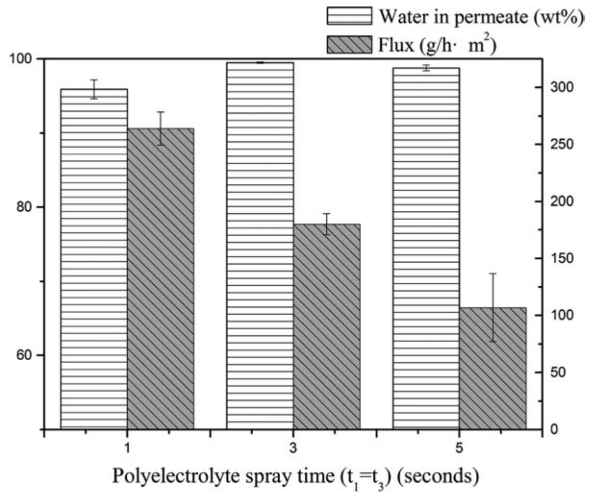

Figure 6. Effects of polyelectrolyte spray time on the pervaporation performances of sprayed multilayer membranes.

(Preparative conditions for spray-LbL assembly: t_2 = 3s, t_4 = 27s, and t_5 = 30 min; 30 bilayers; 0.125 wt % PEI aqueous solution, 0.025 wt % PAA aqueous solutions; 25°C. Pervaporation conditions: feed solution temperature 65°C, down-stream pressure 200 Pa, water content in feed solution 5.0 wt %).

separation factor was achieved using a rinse time of 3 s. When the rinse time was extended to 5 and 7 s, the water content in the permeate decreased a little. Although rinsing was clearly an essential procedure for the achievement of good separating qualities, longer rinse times have the potential to remove the swelled polyelectrolyte and lead to degradation of the separation performance. In addition to the rinsing time, the polyelectrolyte coating time (t_1 and t_3) should also be important to the LbL formation and membrane performance. Figure 6 shows the variation of the pervaporation performance with spraying time. As expected, the flux decreased while the selectivity increased with the increase in the spraying time. The water contents in permeate obtained from both 3 and 5 s were a little higher than that from 1 s.

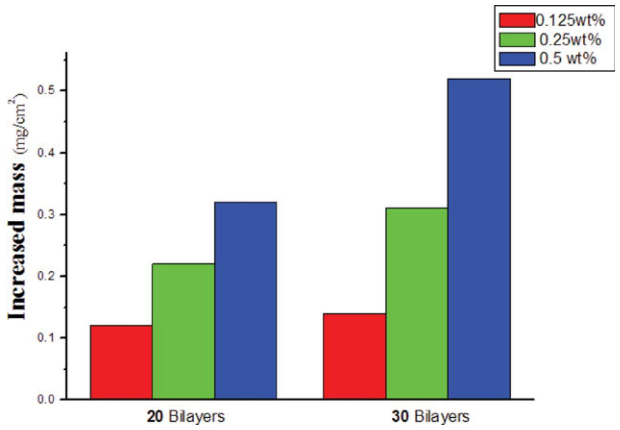

Figure 7. Variations of multilayer mass with PEI concentration (Preparative conditions for spray-LbL assembly: t_1 = 3s, t_2 = 3s, t_3 = 3s, t_4 = 27s, and t_5 = 30 min; 0.025 wt % PAA aqueous solutions; 25°C).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. Effects of the PEI Concentration on Pervaporation Performance

PEI Concentration (wt %)	EtOH Content in Feed Solution (wt %)	Water Content in Permeate (wt %)	Permeate Flux, J (g/h m^2)	Separation Factor, α
0.125	95.0	99.5	180	3781
0.25	95.0	97.2	285	660
0.5	95.0	60.8	506	29

Preparative conditions for spray-LbL assembly: 30 bilayers of PEI/PAA; t_1 = 3s, t_3 = 3s, and t_4 = 27s; 0.025 wt % PAA aqueous solutions; 25°C. Pervaporation conditions: feed solution temperature 65°C, permeate pressure 200 Pa, EtOH content in feed solution 95.0 wt %.

The concentration of polyelectrolyte was also a crucial parameter for the formation of multilayers. Figure 7 represents the evolution of the mass increment per cm^2 for various concentrations of PEI solution while the PAA concentration was kept constant at the value of 0.025 wt %. The multilayer mass was measured using a laboratory electronic weighing balance (accuracy: 0.001 g). Figure 7 shows that, for assemblies with both 20 and 30 bilayers of PEI/PAA, the multilayer mass increased with increasing polyelectrolyte concentration. Table 1 shows the pervaporation performance of multilayer membranes obtained using different PEI concentrations. As shown in Table 1, the water content of the permeate was over 99.0 wt % obtained using the low PEI concentration of 0.125 wt %. However, the water in the permeate was significantly reduced, to 60.8 wt %, when the concentration of PEI was increased to the high value of 0.5 wt %. The permeate flux correspondingly increased to 285 and 506 g/h m^2 as the concentration increased to 0.25 and 0.5 wt %. This suggested that, in addition to the deposition mass, the multilayer structure formed may have a strong

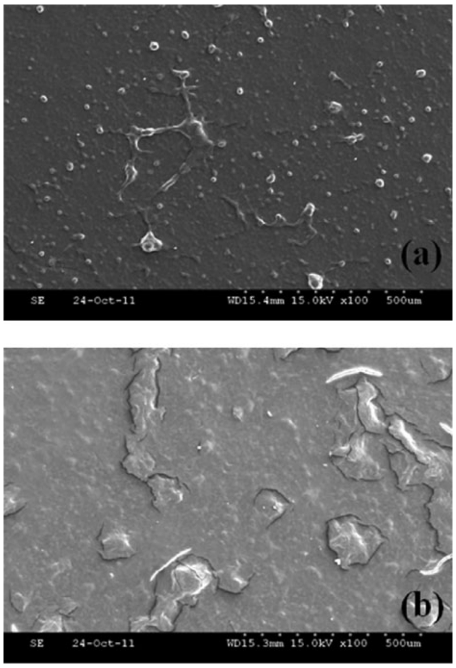

Figure 8. SEM images of multilayer membranes with 30 bilayers of PEI/PAA.

(a) 0.25 wt % PEI aqueous solution (100×). (b) 0.5 wt % PEI aqueous solution (100×). (Preparative conditions for spray-LbL assembly: t_1 = 3s, t_2 = 3s, t_3 = 3s, t_4 = 27s, and t_5 = 30 min; 0.025 wt % PAA aqueous solutions; 25°C).

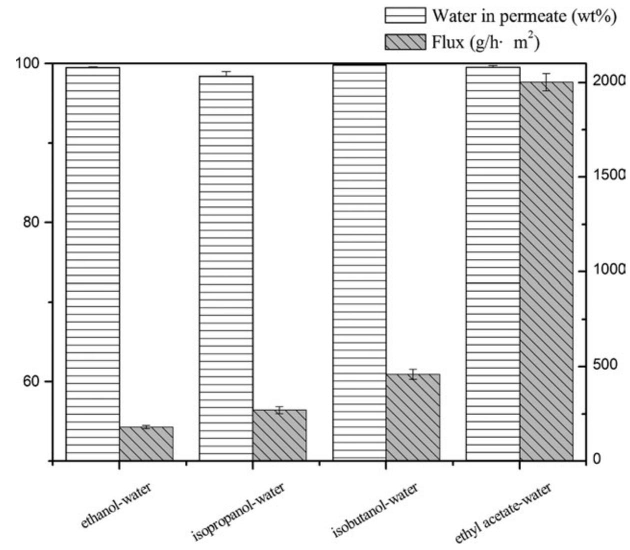

Figure 9. Pervaporation performance of sprayed multilayer membrane for separation of 5 wt % solvent-water mixtures at 65°C.

impact on the separation capability. This is a really interesting observation. To clearly understand the differences in membrane formation with different PEI concentrations, later experiments were evaluated by SEM. As shown in Figure 8, a big lump and crack was formed on the surface at high PEI concentrations, which is the reason that the pervaporation property was worse. Usually, at a low PEI concentration, the polyelectrolytes form a stretched structure, which is beneficial for the formation of a dense and defect-free layer after spraying on the surface. However, at a higher solution concentration, the polyelectrolytes begin to shrink and coil and the defects may easily be formed within the separating layer.

Besides ethanol-water system, the pervaporation performances of sprayed multilayer membranes were also evaluated using different solvent-water mixtures including isopropanol-water, isobutanol-water, acetone-water, and ethyl acetate-water mixtures. The results are shown in Figure 9. It is notable that the sprayed multilayer membrane also shows excellent dehydration performance for the other solvent-water mixtures. Obviously, higher separation performance is obtained with increasing molecular size of the alcohol molecules. Meanwhile, this would facilitate water transport much more rapidly across the membrane to produce high flux. Similar phenomena may have been observed with other polyelectrolyte multilayer membranes.[19] Besides the alcohol-water mixture, this membrane can be used to dehydrate other solvent-water mixtures. For instance, in the case of the pervaporation of a 95.0 wt % ethyl acetate-water mixture, the water content in the permeate and permeate flux reached 99.6 wt % and 2001 g/h m^2, respectively.

Although the use of LbL-assembled multilayer membranes for different separation applications has been widely reported in the literature, one disadvantage is that the fabrication time for the formation of a defect-free selective layer has been too long. Another challenge for the translation of multilayer assembly to industrial applications is the ability to generate these thin film systems sufficiently rapidly. The rapid spray-LbL method appears to be promising for overcoming the above difficulties through control of the arrangement of the misting nozzles and using an automatic system. Table 2 summarizes the whole assembly procedure including the deposition cycle and deposition times for different LbL methods. As shown in Table 2, the classical static dip-LbL assembly usually requires as many as 50–60 bilayers to obtain a defect-free dense membrane, which is a time-consuming process. To simplify the LbL process, we have previously developed a dynamic pressure-driven LbL assembly. This technique was able to significantly reduce the whole process cycle to a few bilayers because the sequential reaction was taking place during the dynamic pressure-driven filtration processes. By comparison, the spray-LbL has mainly focused on the decrease in the deposition time per layer, rather than process cycle, by using misting nozzles. Cycle times for the generation of LbL films using spray-LbL are of the order of tens of seconds, rather than the 20–30 min cycles used in the above three methods. This is because, in the case of the spray assembly, the mass transfer of the polyelectrolyte from the bulk solution to the substrate surface can be enhanced through the spray pressure. Meanwhile, since the polymer is misted into microdroplets during the spraying process, the polycation (polyanion) is able to rearrange much more rapidly on arriving at the negatively (positively) charged surface.[31,32] It is noted from Table 2 that only 90min are needed to complete a 30-bilayer assembly using the spray-LbL process, while still ensuring a high separation capability. Using the spray-LbL process to make a 30-bilayer membrane can lead to a 80-fold decrease in assembly time compared with a classical dip-LbL assembly of 60 bilayers. Although the dynamic LbL that we have previously developed required much fewer deposition cycles compared with the spray-LbL technique, the complete process time for 4 bilayers still needed 440 min, which is about five times higher than for 30-bilayers using the spray process. In addition to the drastic decrease in process time, another advantage is that the spray-LbL assembly technique can easily be accomplished by an automatic system. This will benefit scale-up and lead to highly efficient production.

Conclusions

In this study, the spray-LbL technique was successfully applied to assemble separate layers on to a nanoporous PAN UF membrane. The resulting composite multilayered membrane was used for the pervaporation separation of alcohol/water mixtures. Through this assembly method, the processing time was drastically reduced, while the polyelectrolyte multilayer membranes obtained from 20 bilayers had a flux of 264 g/h m^2 and a separation factor of 423 (feed solution 95.0 wt % ethanol-water, 65°C). The separation factor could be further increased to 3781 with a permeate flux of 180 g/h

Table 2. Comparisons of the Preparation Time of Multilayer Membranes by Different Methods

Method	Multilayer	Deposition Cycles	t_1 (min)	t_2 (min)	t_3 (min)	t_4 (min)	t_5 (min)	T_{total} (min)	Refs.
Classical dip-LbL	PVA/PVS	60	30	30	30	—	—	7200	6,18
Dynamic LbL	PEI/PAA	4	20	5	20	30	30	440	19,20
Spray LbL	PEI/PAA	30	0.05	0.05	0.05	0.45	30	90	This study

m^2 when the deposition was increased to 30 bilayers. Further studies investigated the effects of deposition parameters such as number of PEI/PAA bilayers, rinse time and the solution concentration on the separation behavior. Preliminary studies have indicated that the spray-LbL technology is a feasible and promising method for the preparation of multilayered composite membranes. In addition, because the spray LbL is an attractive technique for scaling-up, LbL-assembled multilayer membranes may prove suitable for many other separation fields such as gas separation and desalination. The spray-LbL technique will contribute towards the preparation of various separation membranes.

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