Dynamic Pressure-Driven Covalent Assembly of Inner Skin Hollow Fiber Multilayer Membrane

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A covalent assembly was accomplished onto hollow fibers via a dynamic pressure-driven layer-by-layer (LbL) technique. The covalent crosslinking multilayers were successfully formed onto the inner surfaces of hollow fiber porous substrates during the alternatively filtration of polyethyleneimine (PEI) and glutaraldehyde (GA) solutions. The formation of covalent bond between PEI and GA was confirmed using fourier transform infrared (FTIR) spectra. The thickness increment on a quartz slide clearly suggested the stepwise growth of multilayer at nanometer scale. The regular alternation of zeta potentials demonstrated that the successful formation of GA-crosslinked PEI multilayers on the hollow fibers. The multilayer membranes showed excellent pervaporation performances for the dehydration of different solvent–water mixtures. The selectivity and permeability can be controlled by varying the PEI layer number. More importantly, the covalent assembled multilayer membrane rendered much higher stabilities compared with those from electrostatically LbL assembly, which offers much opportunity for practical applications. © 2010 American Institute of Chemical Engineers

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Keywords: covalent assembly, dynamic pressure-driven layer-by-layer technique, hollow fiber, glutaraldehyde, pervaporation

Introduction

In recent years, the fabrication of ultrathin polymeric films on solid substrate surfaces with nanometer-control over their properties has received considerable interest due to their potential and/or demonstrated applications such as microcapsules,[1,2] macroscopic sacs,[3] sensitive solar cell films,[4,5] biosensors,[6,7] fuel cell,[8] and separation membranes.[9–12] Among the film fabrication technique established so far, layer-by-layer (LbL) assembly is a versatile method by the alternate immersion of substrates into interactive polymer solutions.[13,14] Particularly, LbL method offers a simple approach to construct selective separation layer onto different types of porous supports, such as flat sheet,[15–17] tubular,[18,19] and hollow fibers.[20,21] The resulting LbL assembled membrane can then be used for the separation of a wide variety of liquid mixtures such as azeotropic, close-boiling point, isomers and/or heat sensitive mixtures,[9–12,15–18,20,21] for ion separation,[22,23] water softening, and desalination[24,25] as well as for size-selective separation of molecules (molecular sieving).[26,27] In the blooming research area of LbL assembled separation membranes, the driving-forces for the assembly applied so far are mostly electrostatic force of aqueous-based oppositely charged polymers. The stabilities of the electrostatically assembled membranes are usually strongly dependent on the feed solution composition due to the relative

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weak electrostatic interaction. For example, we have recently reported that the post-treatments of the weak polyelectrolyte multilayer membranes with salt, acid, and alkali offer much opportunity for the formation of loose structure and big defects on multilayers, which would in turn lead to the deterioration of membrane performance.[28] To improve the stability, a metal–ligand-coordinated multilayer membrane has been recently developed for separation applications in our laboratory.[29] In contrast, covalent bonding may yield much more stable structures. In fact, direct covalent LbL has already been used to the assembly of other functional multilayers such as nanotubes and microcapsules. For instance, Tian et al. have reported a pressure-filter-template approach to prepare fluorescent nanotubes of polyethyleneimine (PEI) and 3,4,9,10-perylenetetracarboxylicdianhydride through covalent combination in the porous of alumina template based on the LbL assembly.[30] Gao and coworkers have developed single polyelectrolyte microcapsules using glutaraldehyde (GA)-mediated covalent LbL assembly. It has been demonstrated that GA can crosslink the adsorbed poly(allylamine hydrochloride) (PAH) or PEI, and introduce free aldehyde group for the next PAH or PEI adsorption on $MnCO_3$ microparticles, thus accomplishing covalent LbL assembly.[1,2] They further carried out the direct covalent LbL assembly on silica particles using poly(glycidyl methacrylate) and PAH as the building blocks. Hollow microcapsules with ultrathin shells and good shell completeness were obtained after core removal. It is noted that the microcapsules have good mechanical strength and stability against extreme pHs and elevated temperature.[31] Caruso and coworkers have developed the LbL assembly of poly(acrylic acid) (PAA) multilayer films using click chemistry. They demonstrated that the click moiety provides stable crosslinks within the films.[32] More recently, Huang and Chang have reported the syntheses of azido- and acetylene-functionalized poly(*N*-isopropylacrylamide) copolymers and their use in the fabrication of ultrathin thermoresponsive microcapsules through direct covalent LbL assembly using click chemistry.[33] Although there is an increasing development of covalent LbL assembly, most of the previous studies focus on the covalent assembled multilayer on rigid substrates such as quartz slides, silicon wafers, and microparticles. The selective separation properties of covalent LbL assembled multilayers on porous substrates remain largely unexplored.

For dense separation membranes, the development of cost-effective membrane modules still remains a major issue. For example, the plate-and-frame is currently still the dominating module configuration used in pervaporation separation processes.[20,21] When compared with the plate-and-frame module, hollow fiber module has some advantageous such as high-packing density, a self-contained mechanical support, a self-contained vacuum channel, and hence the consequent economical superiority.[34–37] Particularly, the construction of selective multilayers onto inner surface of 3-D hollow fiber porous substrates has been the subject of pervaporation separation research. In this case, the hollow fibers, with an integrally defect-free inner layer supported on an open porous substrate, exhibit intrinsic selectivity for a wide variety of liquid mixtures. This type of module may offer advantages such as easy formation of ultrathin selective layer, easy protection of the separation layer, good distribution of feed solution, and low-transport resistance on the permeate side.[20,21,28,29] Recently, a pilot-scale inner skin hollow fiber pervaporation module with a length of 1 m was successfully produced in our laboratory.[21] It suggested that the inner skin hollow fiber pervaporation membranes have great potential for industrial applications. However, it is necessary to seek for effective approaches to improve the stability of electrostatically LbL assembled multilayer membrane.[28]

Herein, we report on the development of dynamic pressure-driven covalent assembly to construct stable crosslinking multilayers onto the inner surface of hollow fiber substrate membranes. Differing from the rigid substrates, in terms of the unique features of polymeric porous substrates such as wide pore diameter distribution and good permeability, dynamic pressure-driven LbL assembly had been recently developed in our laboratory.[20,21,28,29] This technique provides a particularly effective approach for fabricating an ultrathin selective layer by dynamically depositing polymer building blocks onto the porous substrates. Figure 1 shows a schematic illustration of the preparation of a GA-crosslinked PEI multilayer on a polyacrylonitrile (PAN) hollow fiber substrate membrane by dynamic pressure-driven LbL assembly. Before the assembly, the hollow fibers were hydrolyzed by sodium hydroxide solution to create negative charge surface containing carboxyl groups. PEI was firstly assembled onto the inner surface of hollow fiber hydrolyzed PAN porous substrate by a pressure-driven process. The GA solution was then dynamically filtered through the PEI-coated inner surface. In this way, the GA can crosslink and endow the PEI-coated layer with reactive aldehyde groups, by which another PEI layer can be assembled. Alternating multilayer films could be obtained by repeating these two steps in a cyclic fashion. Each added layer is used to cover the defects in prior layers so as to form defect-free selective layer on the inner surface of hollow fibers. Because this approach can be applied, in principle, to other covalent LbL assembly to prepare stable crosslinking multilayers, it will open significant possibilities for the rapid construction of new multilayers on hollow fiber porous substrates, which will be of considerable use in many separation fields.

Experimental Section

Materials

Branched PEI (M_w 60,000) was purchased from Acros. The concentration of PEI aqueous solution was maintained at 0.25 wt %. It was used without pH adjustment and the addition of ionic salt in the assembly process. GA, sodium hydroxide, ethyl acetate, butanol, isopropanol, ethanol, hydrogen peroxide, and sulfuric acid were obtained from Beijing Chemical Factory. The concentration of aqueous GA solution for assembly was 0.5 wt %. Quartz substrates for thickness measurements were purchased from Beijing Kinglass Quartz Co. Hollow fiber PAN ultrafiltration membranes spun by a dry/wet-phase inversion method were used substrates.[38] The inner diameter of each hollow fiber was 1.1 mm. The properties of substrate membranes before and after hydrolysis had previously been reported.[20]

Multilayer build up onto quartz slides

Quartz slides were treated with boiling piranha solution (30:70 v/v H_2O_2:H_2SO_4) for 5 h, followed by rinsing with

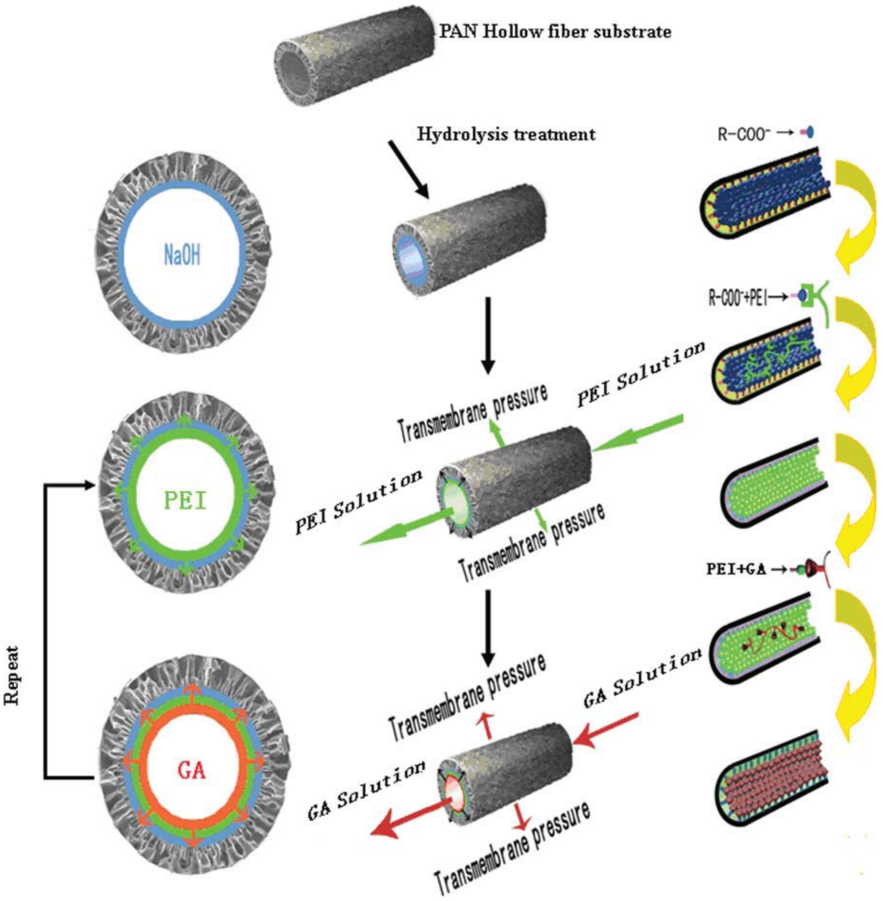

Figure 1. Schematic illustration of the preparation of a GA-crosslinked PEI multilayer on a PAN hollow fiber substrate membrane by dynamic pressure-driven LbL assembly.

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

copious amount of ultrapure water. LbL assembly was performed by sequentially exposing the substrates to PEI and GA aqueous solutions for 30 min. Before the next cycle, the films were extensively rinsed with ultrapure water and dried with a nitrogen flow. Alternating PEI/GA multilayer films could be obtained by repeating these steps in a cyclic fashion.

Multilayer build up onto 3-D hollow fiber hydrolyzed PAN porous substrates

According to the previous studies,[20,21] the PAN hollow fibers were hydrolyzed for 15 min at 65°C by immersing into a 2 mol/L NaOH aqueous solution before assembly. The negatively charged fibers were then put into a polymethylmethcrylate tube with a diameter of 1.5 cm. Both ends of the hollow fiber module were sealed with epoxy resin. The assembly experiments were carried out by using a laboratory fabricated cross-flow negative pressure filtration cell.[20] The PEI and GA solutions were alternatively provided into the lumen side of hollow fiber and then recycled by using two peristaltic pumps and through separate tubings. On the outer surface side, a vacuum pump was used to form a negative pressure of -0.09 MPa. The assembly time for either PEI or GA was 30 min. After each assembly, inner surface of the hollow fiber was rinsed with substantial ultrapure water for 30 min and dried for about 60 min by recycling filtered nitrogen gas.

Pervaporation experiments

The hollow fiber crosslinking multilayer membranes were evaluated by pervaporation separation of different solvent–water mixtures. The measurement systems have been described in our previous studies.[20,21] Of note, a specially designed cross-flow system was used to evaluate the hollow fiber multilayer membrane performance.[20] The feeding solution contacted with the inner surfaces of the hollow fiber modules at 50°C. Three modules with same assembly conditions were examined at each pervaporation condition. The permeate vapor was trapped with liquid nitrogen. The downstream pressure was about 100 Pa. Fluxes were determined by measuring the weight of liquid collected in the cold traps during a certain time under steady-state conditions. The compositions of feeding solutions and permeates were determined with a gas chromatography (GC-14C, SHIMADZU). The separation factor α was calculated from the quotient of the weight ratio of component i and component j in the permeate, Y_i/Y_j, and in the feed, X_i/X_j.

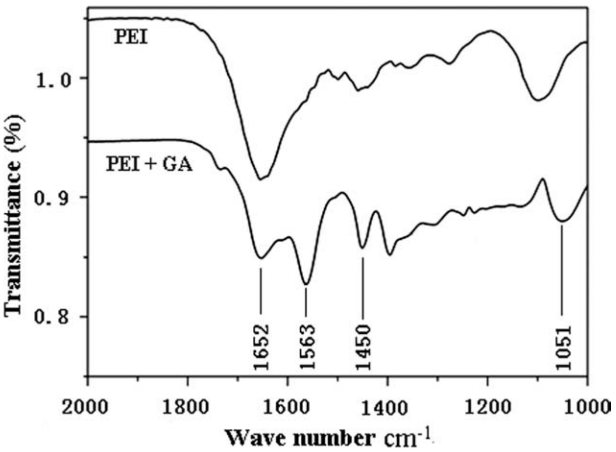

Figure 2. FTIR spectra of PEI before and after GA crosslinking.

$$\alpha = \frac{Y_i X_j}{Y_j X_i}$$

Characterization

FTIR spectra were obtained using a Vertex-70 spectrophotometer (Bruker, Germany). Measurements were carried out at room temperature. The thicknesses of multilayer film assembled on quartz slides were measured using a XP-1 profilometer (Ambios, USA). A groove in the film was made using a razor blade, and the film thickness was estimated by the depth of the groove measured by profilometer stylus. The thickness was recorded thrice at different locations and averaged to yield one data point. Zeta potentials of the hollow fiber inner surfaces were determined using an Electrokinetic analyzer (Anton Paar, SurPASS). In the process for measuring the zeta potential, the KCl solution concentration was maintained at 1.0 mol/L, whereas the operation pressure was 0.03 MPa. A scanning electron microscopy (SEM) (Hitachi-4700, Japan) was used to observe the multilayer morphologies assembled on different substrates. Atomic force microscopy (AFM) images were taken in tapping mode by a AFM (Pico Scan^{TM} 2500, USA).

Results and Discussion

It is well-known that GA has frequently been used as a crosslinking agent due to its low cost, readily availability, and highly solubility in aqueous solution.[39] The GA-mediated assembly of PAH or PEI multilayers on planar substrates and $MnCO_3$ microparticles has previously proved to be feasible.[1,2] In this work, FTIR spectra of PEI and GA-crosslinked PEI were compared with further confirm the covalent driving force for building up films. As shown in Figure 2, a new vibration absorption peak at 1563 cm^{-1}, which is attributable to the ring C—N bonding, appeared in the spectrum of GA-crosslinked PEI product. This clearly confirmed the formation of covalent bonds between GA and PEI because the aldehyde groups of GA can interact with amino groups of PEI molecules.[39] Furthermore, the characteristic peak at 1450 cm^{-1} also provides the evidence for the formation of the stable ring C—C structure in the crosslinked products. The GA-crosslinked PEI multilayer was also assembled onto quartz slides to verify the film growth with layer number. In Figure 3, the film thicknesses are plotted vs. the corresponding numbers of PEI layer. As shown in Figure 3, the linear increase of film thickness with the PEI layer number indicates a progressive deposition of PEI during the assembly. Using profilometer, film thicknesses of 37 nm and 70 nm were calculated for the 8- and 16-layer systems, respectively. Therefore, the average layer thickness was ~4.4 ± 0.2 nm. These results confirm that the GA-crosslinked PEI multilayer can be successfully built up on a planar substrate and the thickness increment can be controlled at the nanometer scale.

Previous studies have demonstrated that the measurement of zeta potential changes is an effective approach to monitor the stepwise growth of polyelectrolyte multilayer according to the variation of electrical properties of the films.[19,28,40] To obtain further evidence for the multilayers formation on the inner surfaces of hollow fiber porous polymeric substrate, inner surface zeta potential was tracked using an electrokinetic analyzer. The zeta potentials of inner surface as a function of the number of PEI layers are shown in Figure 4. It is noted that the PAN surface itself has a weak negative charges of −1.3 mV. After alkaline hydrolysis, the surface potential is thus shifted a more negative value of −4.0 mV due to the formation of the negatively charged carboxylate groups. The charge property of inner surface can change inversely and become positively charged after assembling one PEI layer. Because the charged amide groups of PEI can be crosslinked with aldehyde groups of GA, the positive charges thus decreased after crosslinking reaction. From two- to five-layer surface, the regular alternation of +3.4 mV and +0.1 mV was found after the deposition of PEI and GA crosslinking. These regular changes of the zeta potential

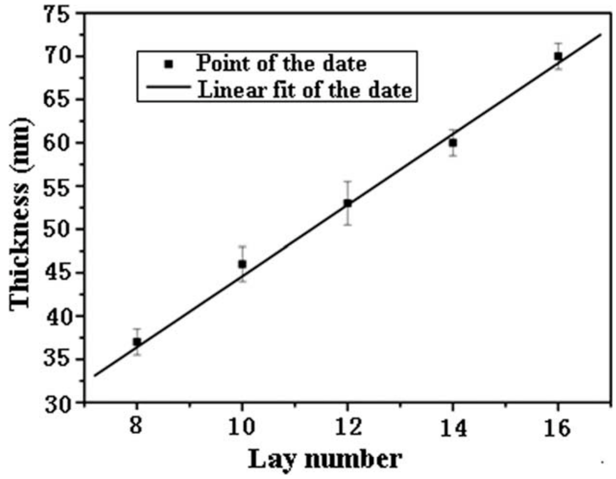

Figure 3. The thickness of GA-crosslinked PEI multilayers deposited on a quartz slide as a function of layer number.

The solid line is a linear fit of the date.

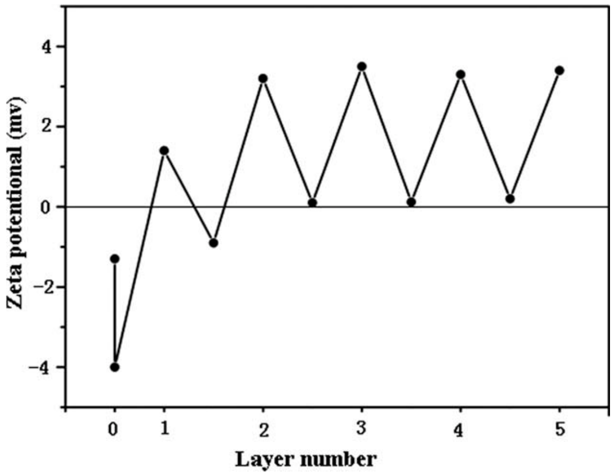

Figure 4. Variations of inner surface zeta potential with layer numbers.

Hydrolysis conditions for hollow fiber PAN support membrane: hydrolysis temperature: 65°C, hydrolysis time 15 min; preparative conditions: 30 min filtration time, 0.5 wt % GA aqueous solution, 0.25 wt % PEI aqueous solution.

indicate the successful stepwise growth of GA-crosslinked PEI layers on the inner surfaces of hollow fiber PAN substrates.

The membrane surface morphologies before and after dynamic LbL covalent assembly were compared by SEM (Figure 5). A number of nanoscale pores were clearly observed on the inner surface of the hydrolyzed hollow fiber PAN membrane substrate (Figure 5a). After pressure-driven assembling with three layers, all the pores on the top surface were completely covered by GA-crosslinked PEI multilayers (Figure 5b). This suggested that a defect-free selective layer was formed. In contrast, the large pores still remained on the outer surfaces of hollow fibers (Figure 5c). It was observed from Figure 5d that the cross-sectional structure of the composite membrane was fingerlike. Therefore, a highly asymmetric hollow fiber composite membrane was successfully achieved (Figure 5d). This asymmetric structure is very important for the selective transport of separation membranes because the outer porous supporting layer generally provides negligible resistance and the separation process is mainly controlled by the ultrathin LbL assembled multilayers. The topography and the surface roughness of multilayer films were evaluated with AFM. Significant changes in surface morphology were also observed for the covalent LbL assembled multilayers (Figure 6). The values of mean roughness (Ra) were obtained based on 20.0 μm × 20.0 μm scan area. The Ra increased with the increase in the layer number. For example, the Ra obtained from one GA-crosslinked PEI layer was only 75 nm. In contrast, the corresponding Ra values are ∼197 nm and 209 nm after assembling three and five GA-crosslinked PEI layers, respectively. This change is attributable to the surface enrichment of GA-crosslinked PEI.

It is anticipated that polymer-based dense separation membranes will contribute to a number of important environmental and energy technologies including fuel ethanol manufacturing, gas separation, and water desalination. Usually, the mass transport across the dense membranes is governed by a solution–diffusion mechanism.[41] This requires the selective layer of the membrane to be nonporous and defect-free. LbL technique provides a general approach to prepare the defect-free selective layer onto porous substrates because the later adsorbed layer can cover the defects in prior layers. However, the LbL process is extremely slow and time consuming, which usually requires as many as 50–60 bilayers.[9,10] Moreover, because the whole substrate is directly immersed into the polyelectrolyte solutions during the traditional LbL process, the multilayers will be formed on both outer and inner surfaces, which increases the transport resistance. Therefore, it is desirable to seek for an effective way to fabricate the defect-free selective layer only on a single side of hollow fibers. The dynamic pressure-driven LbL assembly particularly provides such a unique approach for rapid fabrication of the multilayers on either inner or outer surface of hollow fiber porous substrates. In this work, to obtain the selective multilayer on the inner surface, the PEI and GA solutions were alternatively provided only into lumen side of hollow fibers. Under the action of transmembrane pressure, PEI was firstly filtered through an opposite charge support. When compared with the single static adsorption, the large pores of substrate membrane could be much more easily sealed due to the retention and aggregation of PEI during the pressure-driven process. In the subsequent procedure, the crosslinking reaction between GA and PEI took place during the alternative filtration processes, which in turn resulted in the rapid formation of GA-crosslinked PEI multilayer. Further studies were conducted to examine the selective separation of different solvent–water mixtures. Generally, the layer number plays an important role to achieve high-performance multilayer membrane. Figure 7 shows the variations of pervaporation dehydration performances with the PEI layer numbers in the separation of ethanol- and isopropanol-water mixtures. It was noted that increasing the number of GA-crosslinked PEI layers would lead to the increase of selectivity. For example, the water content could only be enriched from 5 wt % (in the feed) to 50 wt % (in the permeate) for one PEI layer without GA crosslinking in the pervaporation separation of ethanol–water mixture. The water content of the permeate quickly reached 94 wt % ($\alpha = 298$) after GA crosslinking. These values continuously increased to 99.0 wt % ($\alpha = 1881$) and 99.9 wt % ($\alpha = 18981$) as the layer number increased to two and three GA-crosslinked PEI layers. This meant that at least two- to three-layer assembly could achieve relatively high selectivity. Obviously, when compared with the requirement of 50–60 bilayers using traditional LbL technique,[9,10] dynamic pressure-driven covalent LbL technique greatly reduces the cycle numbers of assembly, thus simplifying the LbL procedures. It was also noted from Figure 7 that the total flux decreased with increasing layer number due to the increase in the multilayer thickness. Furthermore, the selective multilayer would become much denser and more compact with the pressure-driven assembly. The similar trend is also observed in the pervaporation dehydration of isopropanol–water mixture. Of note, in this case, both of the higher selectivity and permeability could be obtained. For instance, for only one GA-crosslinked PEI membrane, the water content could be enriched from 5 wt % (in the feed) to 99.9 wt % (in the permeate), whereas the flux maintained at 868 g/(m^2 h) in the dehydration of isopropanol–water mixture (50°C).

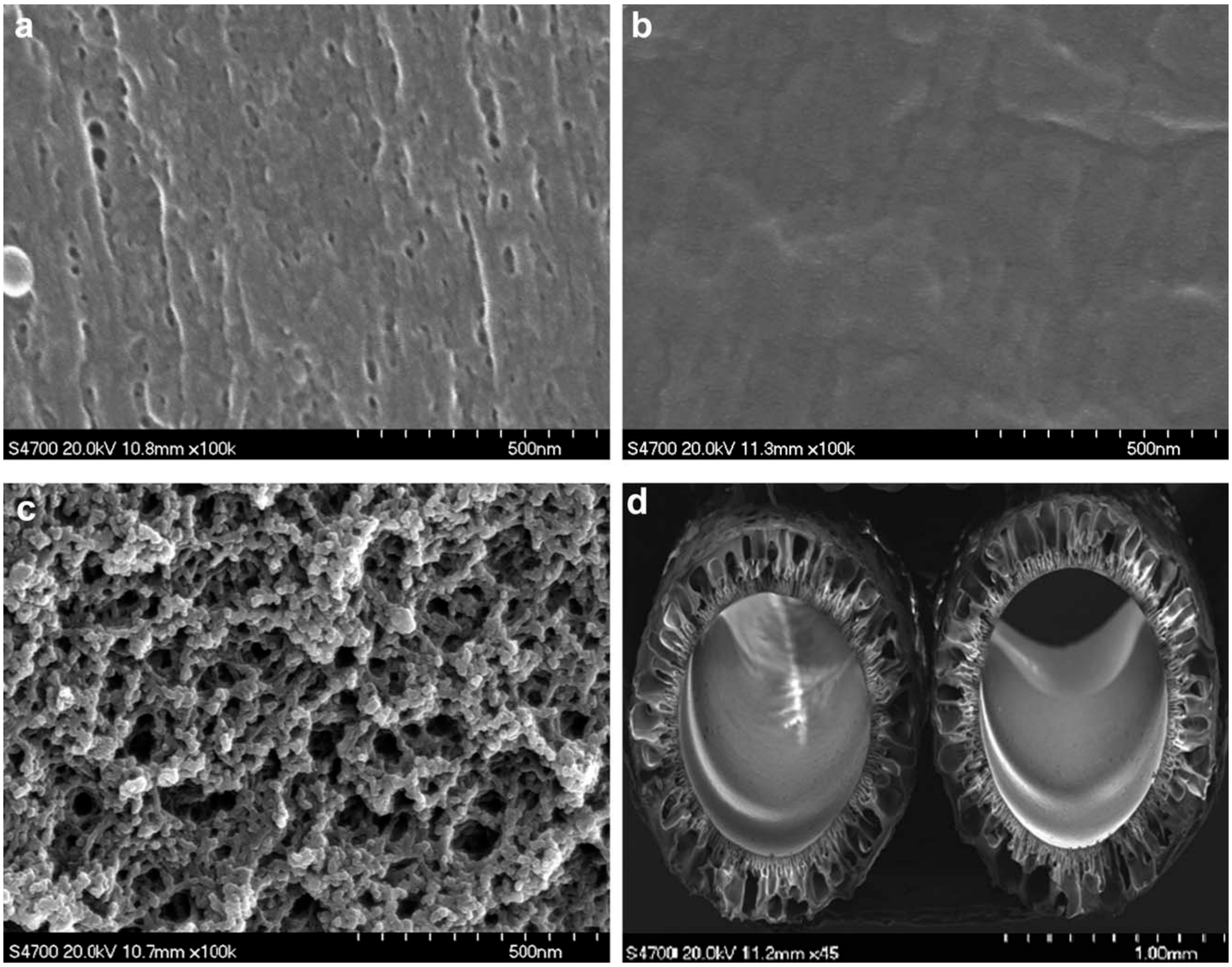

Figure 5. SEM images of (a) the inner surface before assembly (×100k), (b) the inner surface after the assembly of three GA-crosslinked PEI layers (×100k), (c) the outer surface after the assembly of three GA-crosslinked PEI layers (×100k), and (d) overall cross section after the assembly of three GA-crosslinked PEI layers (×45.0).

Figure 8 further shows that the selectivity of multilayer membrane increased with the increase in molecular sizes of alcohol. This is because the strength of the hydrogen bonding decreases with increasing number of carbon atoms in the alcohol. Therefore, water molecules transport much more rapidly across the membrane. Moreover, besides the alcohol–water mixture, the covalent assembled membrane can also be used to separate other solvent–water mixtures. For example, it showed excellent water-pervaporation performance for ethyl acetate–water mixture. In this case, the water content could be enriched from 5.0 wt % (in the feed) to 99.93 wt % (in the permeate), which meant that the separation factor (α) could reach 27,124, whereas the permeate flux was 824 g/(m^2 h) (50°C), respectively.

For commercial separation applications, the membrane stability is one of the key factors to be considered. In our previous study, the stabilities of the electrostatically LbL assembled PEI/PAA multilayer membranes has been reported.[28] It has been demonstrated that the separation performances of hollow fiber polyelectrolyte multilayer membranes were strongly dependent on the composition of the feed solution. Particularly, the salt solution had a great influence on the electrostatically assembled multilayers. Furthermore, because the building blocks of LbL assembled membranes are mostly originated from aqueous hydrophilic polymers, many hydrophilic polymer membranes swell dramatically and even destroy in aqueous solutions.[42,43] Therefore, it is well-recognized that the water swelling is a major issue for the LbL multilayer membranes. In the subsequent experiments, the stabilities of the GA-crosslinked PEI multilayer membrane were investigated. As shown in Figure 9, the flux increased with changing the water content in feed solution from 5 wt % to 40 wt %, whereas the water content in the permeate could be maintained at a constant of 99.9 wt %. For the separation of 40 wt % water–ethanol solution, the permeate flux is up to 1196 g/(m^2 h). It was noted that both the selectivities and stabilities from covalent LbL assembly were much better those from electrostatically LbL assembled PEI/PAA membranes.[28] The reason was that the swelling of the covalently LbL assembled multilayers were much less

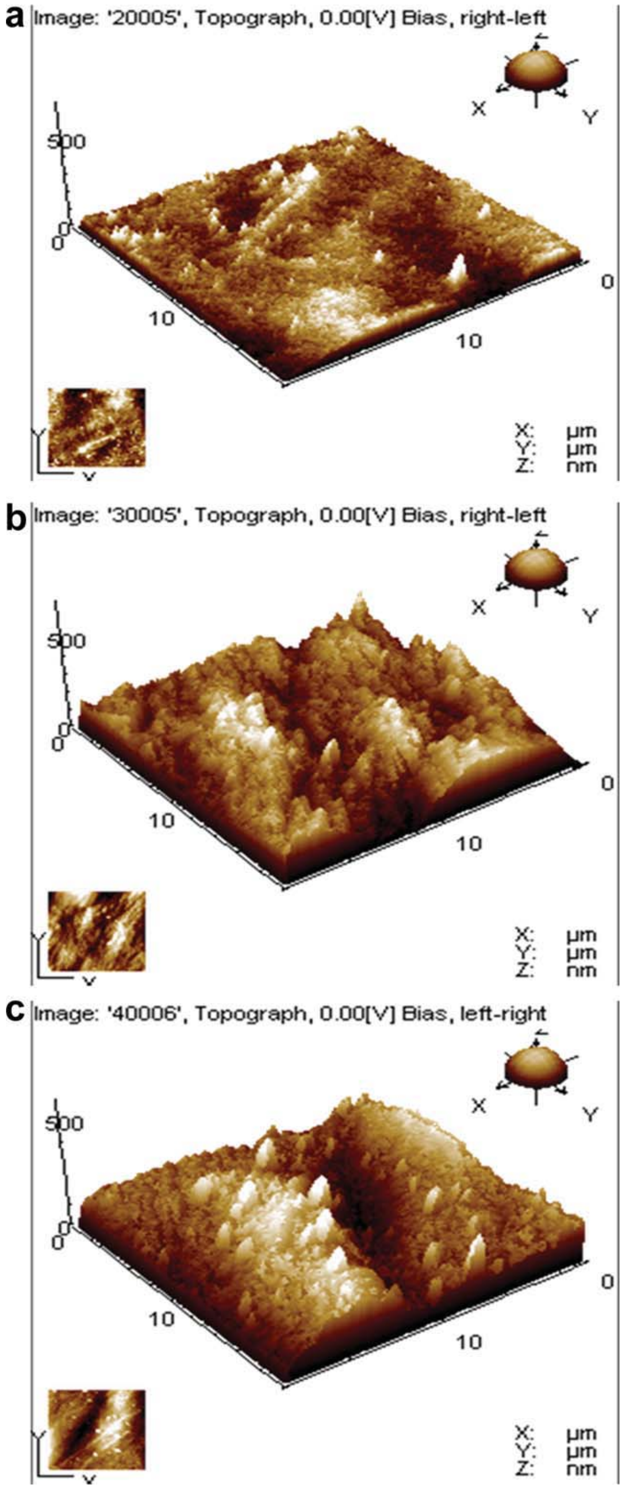

Figure 6. Tapping mode 3-D AFM images of $(PEI/GA)_n$ films with $n = 1$, 3, and 5 (20 μm × 20 μm); (a) $n = 1$, (b) $n = 3$, and (c) $n = 5$.

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

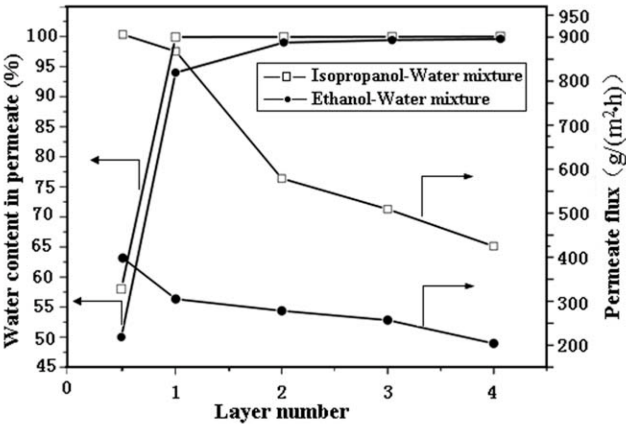

Figure 7. Effects of PEI layer numbers on pervaporation separation performances.

Hydrolysis conditions for PAN support membrane: hydrolysis temperature: 65°C, Hydrolysis time: 15 min. Preparative conditions: negative pressure = −0.09 MPa, 30 min filtration time, 0.5 wt % GA aqueous solution, 0.25 wt % aqueous PEI solution; pervaporation conditions: feed temperature 50°C, permeate pressure 100 Pa, water content in feed solution 5 wt %.

than those electrostatically LbL assembled multilayers because GA provided stable crosslinks within the multilayers. To further investigate the water-, solvent-, and salt-tolerance capacities, three independent hollow fiber multilayer membrane modules obtained from covalent LbL assembly were directly immersed into pure water, isopropanol, and 0.5 mol/L NaCl solutions for 600 h, respectively. The isopropanol dehydration performances were further compared before and after immersion for a certain time. It was noted from Figure 10 that the selectivities were very stable during the operation periods investigated. Even after immersing into either water or isopropanol for over 600 h, the water content in the permeate is still kept over 99.8 wt %. These results strongly suggested that the covalent assembled

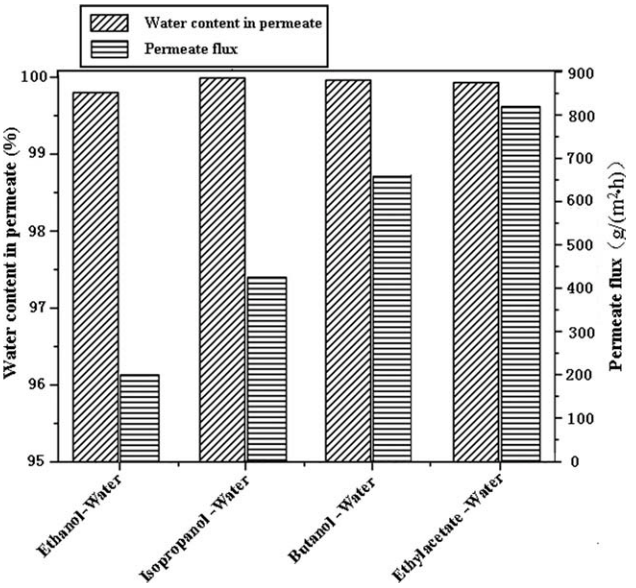

Figure 8. $(GA/PEI)_4$/PAN membrane performance for the pervaporation separation of 95 wt % solvent solutions at 50°C.

membranes exhibit a very good water- and alcohol-tolerance capacities, which could ensure the long-term stability in the separation of solvent–water mixtures. It was also found that the pervaporation performance remained almost unchanged after immersing into NaCl solution for 600 h. As a comparison, our previous study showed that the post-treatment of electrostatically assembled PEI/PAA multilayer membrane with NaCl solution for only 0.5 h would lead to seriously deterioration of membrane performance. Obviously, the covalent assembly is promising approach to prepare a much more stable multilayer membrane for selective separation. The good salt-tolerance capacity of the GA-crosslinked PEI multilayer membrane would offer much opportunity for the potential applications in the pervaporation of real mediums and the water desalination.

Conclusions

In summary, we demonstrate that dynamic pressure-driven covalent assembly can be used for the fabrication of hollow fiber dense separation membranes. To the best of our knowledge, this is the first example to extend the covalent LbL technique to 3-D hollow fiber porous substrates. This approach is unique because the sequential crosslinking reaction takes place during the dynamic pressure-driven filtration processes. One of the most important advantages is that the defect-free selective layer can be achieved on a single side of hollow fiber with only several cycle assemblies. The covalent crosslinking multilayers are more stable than those prepared by the electrostatically LbL approach, which is very important for commercial applications of the dense multilayer membranes. We believe this strategy will prove to be general and important for the preparation of an exciting range of tailored multilayer membranes for studies in separation applications.

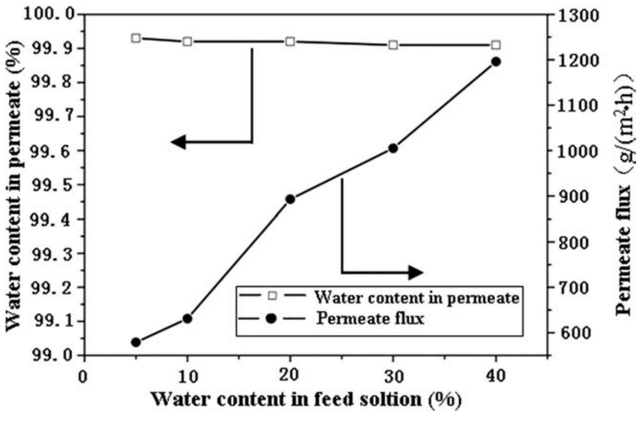

Figure 9. Variation of pervaporation performance with water content in the feed solution at 50°C.

Hydrolysis conditions for PAN support membrane: hydrolysis temperature: 65°C, Hydrolysis time: 15 min. Preparative conditions: two GA-crosslinked PEI layers, dynamic negative pressure: −0.09 MPa, 30 min filtration time, 0.5 wt % GA aqueous solution, 0.25 wt % aqueous PEI solution, 25°C. Pervaporation conditions: feed temperature 50°C, down-stream pressure 100 Pa.

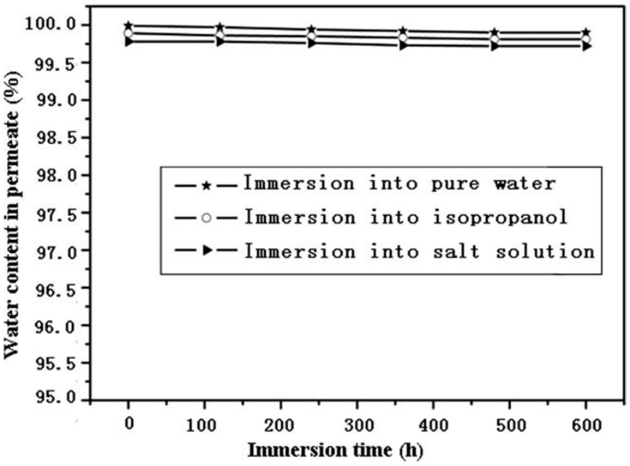

Figure 10. The stabilities of $(GA/PEI)_4/PAN$ membranes after directly immersing into pure water, isopropanol, or NaCl solutions.

Hydrolysis conditions for PAN support membrane: hydrolysis temperature 65°C, hydrolysis time 15 min; preparative conditions: 30 min filtration time, 0.5 wt % GA aqueous solution, 0.25 wt % aqueous PEI solution, dynamic negative pressure −0.09 MPa, 25°C; pervaporation conditions: feed temperature 50°C, permeate pressure 100 Pa, water content in feed solution 5 wt %.

Acknowledgments

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