Dynamic Layer-by-Layer Self-assembly of Organic–Inorganic Composite Hollow Fiber Membranes

Naixin Wang, Guojun Zhang, and Shulan Ji
Center for Membrane Technology, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing, 100124, P.R. China

Yiqun Fan
State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P.R. China

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Multilayer membranes constructed layer-by-layer (LbL) is finding increasing importance in many separation applications. The efficient construction of LbL multilayer on to hollow fiber substrates may offer many new opportunities for industrial applications. An organic–inorganic composite hollow fiber membrane has been developed using a dynamic LbL self-assembly. This poly(acrylic acid)/poly(ethyleneimine) multilayer was dynamically assembled onto the inner surfaces of ceramic hollow fiber porous substrates pretreated by Dynasylan Ameo silane coupling agents. The hollow fibers were subsequently heat crosslinked to obtain stable permselective membranes. The formation of multilayers on the hollow fibers was characterized with a SEM, EDX, an electrokinetic analyzer and IR spectra. The effects of layer number, feed temperature and water content in the feed on the pervaporation performance have been investigated. To the best of our knowledge, this is the first report of LbL assembly of polymer building blocks onto ceramic hollow fiber porous substrates.
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Keywords: organic–inorganic composite membrane, hollow fiber, layer-by-layer, self-assembly, pervaporation

Introduction

Dense membrane separation has been widely used in many fields, such as fuel ethanol manufacturing,[1] recovery of organic solvent,[2] water purification,[3] gas and hydrocarbon separation.[4–7] The development of new membrane materials and efficient membrane modules is still the central task in this field. Usually, the dense membrane is fabricated by coating a defect-free selective dense layer on to a porous support. The alternating layer-by-layer (LbL) deposition of positively and negatively charged polymers on to porous supports has proven to be a versatile tool for the creation of new dense composite membranes. One clear advantage is that each added layer is used to cover the defects in previous layers. Previously, it has been demonstrated that LbL-assembled composite membranes can function for a wide range of uses such as pervaporation,[8–10] gas separation,[11] nanofiltration,[12] reverse osmosis[13] and forward osmosis.[14] However, most previous work has focused on the LbL assembly of polyelectrolyte multilayers on a planar porous support. For separation applications, hollow fibers are well recognized as the most cost-effective membrane modules due to their high-packing density. Therefore, the construction of a polyelectrolyte multilayer on to hollow fibers has great potential for industrial use. In our laboratory, a hollow fiber polyelectrolyte multilayer membrane has been successfully fabricated by alternately filtering poly(acrylic acid) (PAA) and polyethyleneimine (PEI) through a hydrolyzed hollow fiber polyacrylonitrile (PAN) membrane under negative pressure.[15] A pilot-scale hollow fiber pervaporation module with a length of 1 m has been successfully produced.[16] For such membranes, although a high separation factor can be easily obtained with several cycles of PAA and PEI deposition, the permeation flux was relatively low. Meanwhile, the PAN support membrane shows low-mechanical strength due to the alkaline hydrolysis treatment.[17] In addition, the weak polyelectrolyte multilayer can become unstable and break up because of the high-salt concentrations and extreme pH values.[18]

An organic–inorganic composite membrane with a thin and dense separation layer on top of porous ceramic substrates combine the advantages of both polymeric and ceramic membranes.[19,20] The ceramic porous substrates provide mechanical and chemical stability, while the polymeric layer is responsible for selective separation. Because of the availability of numerous kinds of organic polymeric materials, many different composite membranes could be prepared for use in different fields. Recently, some researchers have studied organic–inorganic composite membranes. Cohen et al. prepared asymmetric tubular alumina-supported PVAc and PVP membranes for the pervaporation separation of binary mixtures of methanol and methyl tertbutyl ether

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Correspondence concerning this article should be addressed to G. Zhang at zhanggj@bjut.edu.cn.

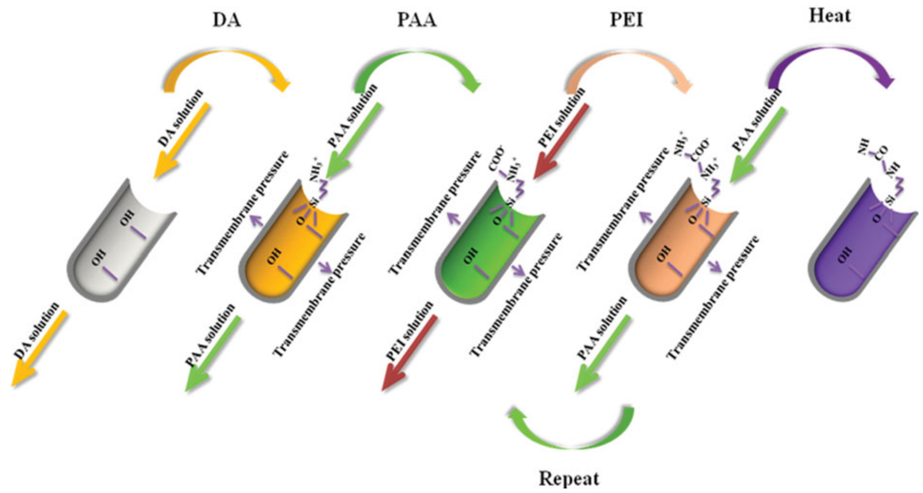
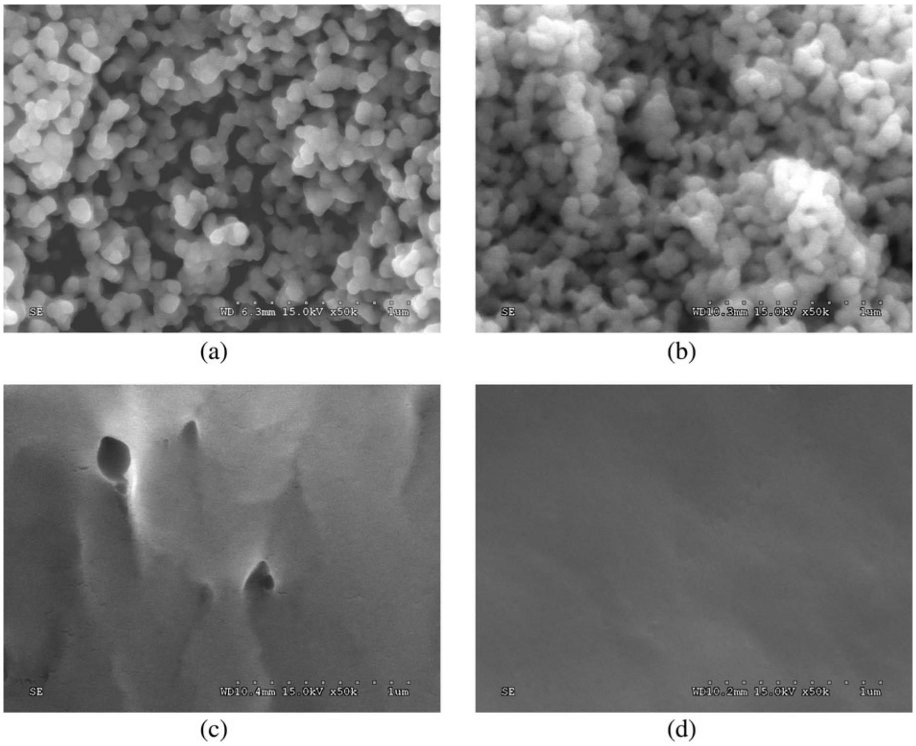


Figure 1. Schematic illustration of the preparation of a multilayer on a ceramic hollow fiber substrates membrane by dynamic pressure-driven LbL assembly.

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

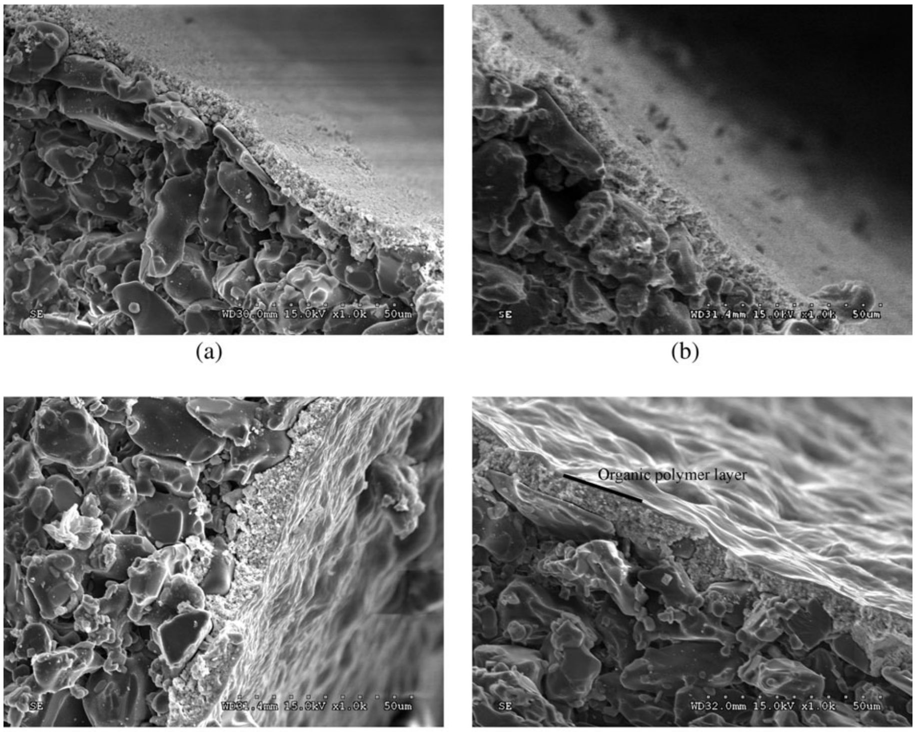
(MTBE). The methanol separation factors for the PVP and PVAc-grafted pervaporation membranes reached values of 26 and 100, respectively, and the maximum flux was 6190 g/m^2 h.[20] Jin et al. reported the preparation of a hydrophobic polydimethylsiloxane/ceramic composite membrane, which has high-pervaporation performance for the recovery of ethanol from its aqueous solution. It was observed that the PDMS/ceramic composite membrane showed a high-total flux of 19500 g/m^2 h and selectivity of 5.7 for ethanol to water at an ethanol concentration of 4.3 wt %.[21] Jin et al. also prepared a PEI-PVS/ceramic composite pervaporation membrane by a self-assembly method. The composite membrane made up of 60 layer pairs of polyelectrolyte showed a high flux of 18400 g/m^2 h, with a water concentration enhancement from 6.2 to 35.3 wt %.[22] Most of the previous studies have suggested that the organic–inorganic composite membrane usually has high flux but the separation factor is unsatisfactory. In order to obtain excellent pervaporation performance for the separation of organic/water mixtures, it is crucial to form a dense and united polymeric layer on the



(a)
(b)
(c)
(d)

Figure 2. SEM images of the inner surface ceramic hollow fiber membranes before and after assembled by a dynamic layer-by-layer technique (×50.0 k); (a) ceramic substrate, (b) pretreated by silane coupling agents, (c) assembly of five layers, and (d) 180°C heat crosslink.

Pretreatment condition: 0.1 mol/L DA solution, pretreatment time 2 h; preparative condition: 5 bilayers, 30 min filtration time, 0.25 wt % PEI aqueous solution, 0.05 wt % PAA aqueous solution, dynamic negative pressure −0.09 MPa, 25°C; crosslink condition: crosslink time 2 h, 180°C; pervaporation condition: permeate pressure 100 Pa, feed temperature 75°C.



(a) (b)

(c) (d)

Figure 3. SEM images of cross-sectional ceramic hollow fiber membranes before and after assembled by a dynamic layer-by-layer technique; (a) ceramic substrate (×1.0 k), (b) pretreated by silane coupling agents (×1.0 k), (c) assembly of five layers (×1.0 k), (d) 180°C heat crosslink (×1.0 k).

Pretreatment condition: 0.1 mol/L DA solution, pretreatment time 2 h; preparative condition: 5 bilayers, 30 min filtration time, 0.25 wt % PEI aqueous solution, 0.05 wt % PAA aqueous solution, dynamic negative pressure −0.09 MPa, 25°C; crosslink condition: crosslink time 2 h, 180°C; pervaporation condition: permeate pressure 100 Pa, feed temperature 75 °C.

ceramic substrates. In particular, for hollow fiber ceramic substrates, it is relatively difficult to obtain a uniform and defect-free inner skin on the hollow fiber using the conventional dip-coating method.

In this work, an organic–inorganic composite membrane has been prepared by alternate deposition of polyelectrolyte on to the inner surface of a hollow fiber ceramic ultrafiltration membrane using a dynamical layer-by-layer technique. Materials for ceramic preparation have usually been Al_2O_3, TiO_2, ZrO_2 and SiO_2. They may have surface hydroxyl groups, which readily react with some organosilanes,[23] which can then be used to introduce some specific functionality to the surface of the ceramic membrane. The ceramic substrates can then be modified by a polymer layer.[19] As shown in Figure 1, the ceramic hollow fiber substrate membranes were modified by Dynasylan Ameo silane coupling agents which contain an amino group in the molecular formula. The silane group reacts with the hydroxyl groups found on the ceramic surface to form siloxane bonds (-Si-O-ceramic) through a condensation reaction. The siloxane bonds can form a stable structure on the surface of the ceramic membrane.[24,25] After pretreatment by the Dynasylan Ameo silane coupling agents, the PAA/PEI multilayer can be successfully assembled on to the inner surface of the ceramic hollow fiber membranes through dynamic electrostatic LbL assembly. After several pairs of polyelectrolyte layers have been assembled on the ceramic hollow fibers, the organic–inorganic composite membranes were heated to effect crosslinking at the appropriate temperature. The crosslinking of the PAA/PEI systems via heat-induced amide formation from carboxylate-ammonium complexes can strengthen the multilayer.[26] To our best knowledge, this is the first work describing the LbL assembly of polymer building blocks on to ceramic hollow fiber porous substrates.

Experimental Section

Materials

Poly(acrylic acid) (PAA, Mw 4,000,000) and 3-Aminopropyl-trimethoxysilane (Dynasylan Ameo silane coupling agents, Mw 179.29) were obtained from Aldrich. Branched poly(ethyleneimine) (PEI) with a molecular weight of 60,000 was purchased from ACROS. Ethanol was provided by the Beijing Chemical Factory. The chemicals were all used as received without further purification. The hollow fiber ceramic substrate membranes were provided by Nanjing University of Technology with average pore sizes of 50 nm. The inner diameter and outer diameter of each hollow fiber was 2 mm and 4 mm, respectively. The inner dense layer was prepared from ZrO_2, and the outer support layer was prepared from Al_2O_3.

Multilayer buildup onto the hollow fiber ceramic membrane

The hollow fiber ceramic membranes were pretreated by Dynasylan Ameo silane coupling agents before assembly. The pretreatment on the hollow fiber ceramic membrane surface consists of two steps. First, the hollow fiber ceramic substrate membrane was immersed in the mixture of ethanol (EtOH) solution (EtOH:H_2O = 95:5) plus 2 g/L

Table 1. EDX Analytical Results of Elements in the Surface of Ceramic Hollow Fiber Membrane

	Elements content (wt %)					
	C	O	N	Si	Zr	Al
Inner surface of ceramic hollow fiber substrate membrane	8.85	30.75	0	0	60.40	0
Inner surface of ceramic hollow fiber membrane after pre-treatment	14.77	30.30	1.76	3.55	49.62	0
Inner surface of ceramic hollow fiber membrane after assembly	36.20	25.52	29.59	0.43	8.26	0
Outer surface of ceramic hollow fiber membrane after assembly	5.74	43.74	9.01	2.02	1.33	38.15

Pretreatment condition: 0.1 mol/L DA solution, pretreatment time 2 h; preparative condition: 30 min filtration time, 0.25 wt % PEI aqueous solution, 0.05 wt % PAA aqueous solutions, dynamic negative pressure −0.09 MPa, 25°C.

DA silane coupling agent at room temperature for 2 h. Ethanol was chosen due to its strong interaction with water and its relatively benign nature. Second, the substrate was washed with deionized water. Then, the modified substrate was dehydrated at 110°C for 2 h in a vacuum oven to remove the adsorbed water vapor or other organic vapors before assembly. The pure water flux across the ceramic hollow fiber membrane before and after pretreatment was characterized.

Solutions of 0.25 wt % PEI and 0.05 wt % PAA were prepared. The preparation of PEMMs on a grafted ceramic hollow fiber membrane was conducted by using a dynamic negative LbL technique, which has been reported in our previous studies.[15,16] The PAA and PEI solutions were alternatively provided into the inner channel of hollow fiber and then recycled by using two peristaltic pumps and through separate tubings. On the outer surface side, a water circulated vacuum pump (SHB-3A, Zhengzhou Greatwall Scientific Industrial and Trading Co., Ltd.) was used to form a negative pressure of −0.09 MPa. The assembly time for either PEI or PAA 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. Upon the formation of PEMMs, they were heat crosslinked in a vacuum oven at different crosslinling temperatures for 2 h.

Pervaporation experiments

The hollow fiber module for the pervaporation test consisted of one fiber with an effective length of 8 cm and effective area of 5.0 cm^2. The hollow fiber modules were mounted on to a laboratory fabricated pervaporation system with the lumen side as the feed side and the shell side as the permeate side. Three modules, prepared and modified in exactly the same way, were examined for each pervaporation condition. The permeate vapor was trapped with liquid nitrogen. The experiments were carried out at a down-stream pressure of 100 Pa produced by a vacuum pump. Fluxes were determined by measuring the weight of liquid collected in the cold traps over a measured time under steady-state conditions. The composition of the collected permeate was determined by gas chromatography (GC-14C, SHIMADZU). The separation factor was calculated from the quotient of the weight ratio of water and alcohol in the permeate Y_{HOH}/Y_{ROH}, and in the feed X_{HOH}/X_{ROH}

$$\alpha = \frac{Y_{HOH}/Y_{ROH}}{X_{HOH}/X_{ROH}}$$

Characterization

A scanning electron microscope (SEM), with a Hitachi S-4300 attached to an energy dispersive X-ray (EDX) unit, was used for observation of the morphologies and determination of the elemental components of the ceramic-based hollow fiber polyelectrolyte multilayer membranes (5 bilayers). All membrane samples were dried under a vacuum. The attenuated total reflectance FTIR spectra (Vertex-70, Bruker, Germany) was used to characterize the changes of morphology of

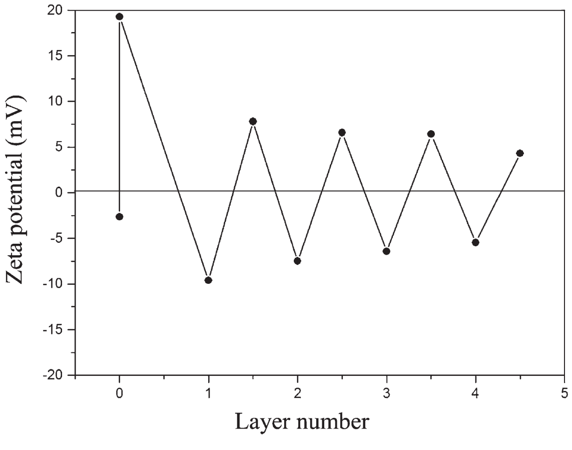


Figure 4. Variations of inner surface zeta potential with layer numbers.

Pretreatment condition: 0.1 mol/L DA solution, pretreatment time 2 h; preparative condition: 30 min filtration time, 0.25 wt % PEI aqueous solution, 0.05 wt % PAA aqueous solutions, dynamic negative pressure −0.09 MPa, 25°C.

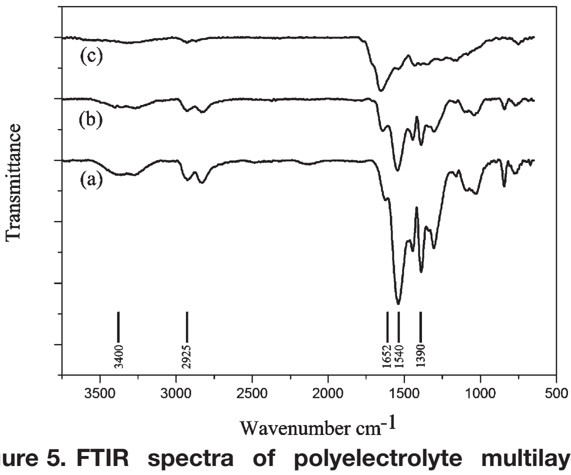


Figure 5. FTIR spectra of polyelectrolyte multilayers assembled on the quartz substrates before and after heat treatment; (a) polyelectrolyte multilayers before heat treatment, (b) polyelectrolyte multilayers crosslinked at 180 °C, and (c) polyelectrolyte multilayers crosslinked at 250°C.

Table 2. Comparison of Polyelectrolyte Composite Membrane Pervaporation Performance with Different Substrates and Methods

Membrane type	Temperature (°C)	Water content in permeate (%)	Permeate flux (g/m^{2}h)	References
PAN/ (PEI/PAA)$_4$/PEI	50	92.8	290	[15]
PAN/PEI/(PSS(Co)$_{1/2}$/P4VP)$_2$	60	99.5	250	[29]
PAN/(PEI/GA)$_4$	50	99.9	190	[30]
Ceramic/ (PAA/PEI)$_5$	75	51.7±1.8	3648±160	This study
Ceramic/ (PAA/PEI)$_5$ (160 °C cross linking)	75	91.7±0.9	1480±115	This study
Ceramic/ (PAA/PEI)$_5$ (180 °C cross linking)	75	97.5±0.6	1050±125	This study
Ceramic/ (PAA/PEI)$_5$ (200 °C cross linking)	75	97.8±0.3	872±68	This study
Ceramic/ (PAA/PEI)$_5$ (230 °C cross linking)	75	97.9±0.3	804±67	This study
Ceramic/(PAA/PEI)$_5$ (250 °C cross linking)	75	98.1±0.3	645±60	This study

Pretreatment condition: 0.1 mol/L DA solution, pretreatment time 2 h; preparative condition: 30 min filtration time, 0.25 wt % PEI aqueous solution, 0.05 wt % PAA aqueous solution, dynamic negative pressure −0.09 MPa, 25 °C; crosslink condition: crosslink time 2 h; pervaporation condition: permeate pressure 100 Pa, water content in feed solution 5 wt %.

the multilayers assembled on quartz substrates (10.5 bilayers). The zeta potentials were determined using an electrokinetic analyzer (SurPASS, Anton Paar). A cylinder cell is used to characterize the hollow fibers. In the process of measuring the zeta potential, about 0.5 mL KCl solution (1 mol/L) was added to 600 mL pure water to form electrolyte solution. The actual concentration of the electrolyte maintained about 0.83 mmol/L while the operating pressure was 0.03 MPa. Measurements were carried out at room temperature.

Results and Discussion

The inner surface and cross-sectional morphology of the ceramic substrate before and after assembly is shown in Figures 2 and 3, respectively. In Figure 2a, we can see many pores on the inner surface of the ceramic substrate. When pretreated by the silane coupling agents, although the silane coupling agents were grafted on to the ceramic substrate by a condensation reaction, the ceramic substrate morphology did not significantly change (Figure 2b and Figure 3b). After assembly using the polyelectrolyte PAA/PEI, most areas of the ceramic substrate surface were covered by the polyelectrolyte. However, there are still some large defects on the multilayer (Figure 2c). This is the reason why the pervaporation performance of the ceramic hollow fiber composite membrane was not good before the crosslinking. When the composite membrane was heated to affect the crosslinking, we can see clearly, from Figure 2d, that a dense and defect-free selective layer is formed on the support membrane. Comparing the cross-sectional SEM Figure 3a,b,c,d), it is clear that an organic polymer layer has been successfully formed on the surface of the ceramic substrate. This cross-linked selective multilayer plays a crucial role for subsequent separation.

Dynasylan Ameo silane coupling agents contain inorganic and organic moieties in the same molecule. The silane coupling agent acts as an interface between the inorganic substrate and an organic material. To understand the role of Dynasylan Ameo silane coupling agents and the assembly of the polyelectrolyte on the hollow fiber ceramic membrane, EDX measurements before and after assembly were performed. As shown in Table 1, the elements N and Si were not found on the inner surface of the ceramic hollow fiber substrate membrane. However, after pretreatment with the silane coupling agent, both N and Si were detected. Meanwhile, the pure water flux across the ceramic hollow fiber decreased from 2865 L/m^2 h to 1281 L/m^2 h. The hollow fiber ceramic membrane was, therefore, proved to have been modified by

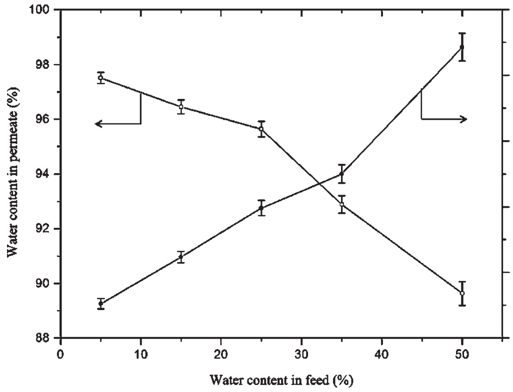


Figure 6. Effect of polyelectrolyte layer numbers on separation factor and flux.

Pretreatment condition: 0.1 mol/L DA solution, pretreatment time 2 h; preparative condition: 5 bilayers, 30 min filtration time, 0.25 wt % PEI aqueous solution, 0.05 wt % PAA aqueous solution, dynamic negative pressure −0.09 MPa, 25°C; crosslink condition: crosslink time 2 h, 180°C; pervaporation condition: permeate pressure 100 Pa, feed temperature 75°C, water content in feed solution 5 wt %.

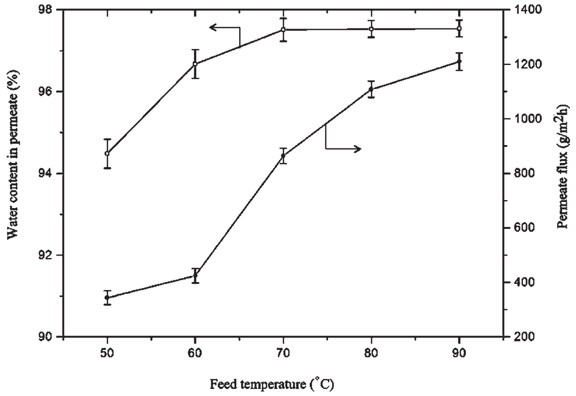


Figure 7. Effect of feed temperature on pervaporation performance.

Pretreatment condition: 0.1 mol/L DA solution, pretreatment time 2 h; preparative condition; 5 bilayers, 30 min filtration time, 0.25 wt % PEI aqueous solution, 0.05 wt % PAA aqueous solution, dynamic negative pressure −0.09 MPa, 25°C; crosslink condition: crosslink time 2 h, 180°C; pervaporation condition: permeate pressure 100 Pa, water content in feed solution 5 wt %.

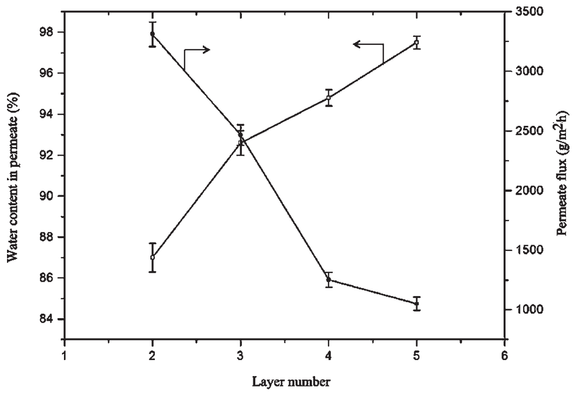


Figure 8. Effect of water content in feed solution on pervaporation performance.

Pretreatment condition: 0.1 mol/L DA solution, pretreatment time 2 h; preparative condition: 5 bilayers, 30 min filtration time, 0.25 wt % PEI aqueous solution, 0.05 wt % PAA aqueous solution, dynamic negative pressure −0.09 MPa, 25°C; crosslink condition: crosslink time 2 h, 180°C; pervaporation condition: permeate pressure 100 Pa, feed temperature 75°C.

the silane coupling agents. When the ceramic substrate is assembled using the polyelectrolyte, the content of the elements N and C increased from 1.76 wt % and 14.77 wt % to 29.59 wt % and 36.20 wt %, respectively. This provides evidence that the organic polymer was deposited on the inner surface of the ceramic hollow fiber substrates.

To obtain further evidence for multilayer formation on the inner surfaces of the hollow fiber porous ceramic substrate, the inner surface zeta potential was tracked using an electrokinetic analyzer. The zeta potentials of the inner surface as a function of the number of polyelectrolyte layers are shown in Figure 4. It is noted that the ceramic surface itself has a weak negative charge of −2.4 mV. After pretreatment by the silane coupling agents, the surface potential is shifted to a more positive value of +19.2 mV due to the formation of the positively charged amino group. The charge on the inner surface can be reversed, so becoming negatively charged, after assembling one PAA layer. The zeta potential changes between +7 and −7 mV when PEI or PAA forms the outer layer, respectively. The reversal of the sign of the zeta potential indicates the stepwise growth of PEI and PAA on the hollow fiber ceramic substrates.

Although the LbL membrane assembly technique has attracted considerable attention and membranes have been investigated for different separation uses, no important practical application has yet emerged. The main reason is that the LbL process involves numerous deposition and rinsing steps, and this complexity greatly limits the potential applications of multilayer coatings. In particular, the presence of only weak electrostatic forces has limited the stability of multilayer for use as a really complicated separation medium. Compared with polymer substrates, ceramic hollow fibers have the advantage of high temperature tolerance. Therefore, simple thermal crosslinking can be used to generate the covalent bond and in turn improve the stability of the multilayer membrane. In the case of the assembly of the PAA/PEI multilayer, the thermal treatment may form an amide bond between the carboxylate and amine groups. In order to demonstrate the effect of heat crosslinking, the FTIR spectra of polyelectrolyte multilayers before and after heat treatment were investigated. As shown in Figure 5, there are peaks at 1,390 cm^{-1} and 1,540 cm^{-1} assigned to the asymmetric and symmetric carboxylate stretch, respectively, which have weakened after heat treatment. This is because the concentration of the carboxylate functional groups in the multilayer has decreased. The amine group at 2,925 cm^{-1} decreased while the amide I at 1,652 cm^{-1} increased. These changes suggested the formation of amide bonds between PEI and PAA due to the presence of the carboxylate and amine groups.[27,28]

The pervaporation performance of the polyelectrolyte composite membrane with different substrates and methods are compared in Table 2. In our previous studies, a polyelectrolyte composite membrane was prepared by the layer-by-layer technique using different driving forces such as electrostatics,[15] metal-ligand-coordination[29] and the covalent force.[30] All the polyelectrolyte pairs were assembled on to the organic polymer substrates. As shown in Table 2, the polyelectrolyte multilayer assembled on organic polymer substrates has a high-separation factor, but the permeate flux was relatively low. In particular, the thermal crosslinked organic–inorganic composite membranes demonstrated relatively good pervaporation performance regarding both separation factor and permeate flux for the dehydration of ethanol. For example, the ceramic/ (PAA/PEI)$_5$ showed a flux of 1050 g/m^2 h and a separation factor of 503. In addition, the effect of the temperature of crosslinking was investigated. The organic–inorganic composite membranes were crosslinked in a vacuum oven at 160°C, 180°C, 200°C, 230 or 250°C with the results shown in Table 2. It is noted that higher crosslinking temperature would benefit for the better selectivity. For example, the water content in permeate at 180°C was significantly higher than the corresponding values associated with 160°C. When the crosslinking temperature was increased from 180 to 250°C, the permeate flux decreased significantly while the water content in permeate increased a little. Consequently, it was decided that 180°C was the appropriate temperature for crosslinking to obtain the best separation performance.

The pervaporation performances with different numbers of PAA/PEI layers are shown in Figure 6. It was noted that increasing the number of deposited PAA/PEI layers led to the increase of the water content in permeate. For example, the water content in permeate was 87.0 wt % for two PAA/PEI layers but quickly reached 97.5 wt % for five PAA/PEI layers. Simultaneously, the total flux decreased from about 3312 g/m^2 h to about 1050 g/m^2 h for the five-bilayer sample. Clearly, the inner skin layer became denser and more compact with the increase in the number of polyelectrolyte layer pairs.

The PEMMs assembled by dynamic LbL on a pretreated ceramic hollow fiber membrane were evaluated within a relatively wide range of feed temperatures and water contents in the feed solution. As can be seen from Figure 7, both permeate flux and water content in permeate increased with increasing operating temperature. Compared with the pure polymer hollow fiber membrane, the polymer multilayer assembled on ceramic substrates can be operated at a higher temperature. When the feed temperature changed from 50 to 90°C, the permeate flux and water content in permeate increased from 345 g/m^2 h and 94.5 wt % to 1210 g/m^2 h and 97.6 wt %, respectively. The increases in the water vapor pressure on the feed side and the diffusion coefficients caused the increase of flux, while the increase in selectivity was because the increase in diffusional selectivity of water was more significant than that of alcohol for the higher feed temperature.

Figure 8 shows the pervaporation separation of an ethanol/water system with water content ranging from 5 to 50 wt %. It is noted that the permeate flux greatly increased from 1050 g/m^2 h to 8900 g/m^2 h, while the water content in permeate decreased from 97.5 wt % to 89.4 wt %. This is because the polyelectrolyte multilayer might have swelled due to the increase of water content in the feed.

Conclusions

In summary, a ceramic-based organic–inorganic hollow fiber composite membrane was successfully prepared using a dynamic layer-by-layer self-assembly technique. It was demonstrated that the organic polymer can be deposited on the inner skin of a ceramic hollow fiber substrate. The process of assembly was characterized by EDX, SEM and an electrokinetic analyzer. It was noted that the organic–inorganic hollow fiber composite membrane shows excellent pervaporation performance for the separation of ethanol/water. The membrane obtained with five bilayers had a permeate flux of 1050 g/m^2 h, while the water content in permeate was 97.5 wt %. Compared with an organic polymer based membrane, the permeate flux was significantly improved while the selectivity still remained at a relatively high level when using the ceramic hollow fiber substrate. Furthermore, the mechanical, chemical and thermal stability of the composite membrane can be enhanced. As a large number of other organic polymer species can be potentially assembled on to a ceramic hollow fiber porous support, this opens a new way to create a series of LbL-assembled organic–inorganic composite hollow fiber membranes for different uses.

Acknowledgments

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Literature Cited

1. Lewandowicz G, Białas W, Marczewski B, Szymanowska D. Application of membrane distillation for ethanol recovery during fuel ethanol production. *J Membr Sci*. 2011;375:212–219.
2. Schlosser Š, Kertész R, Marták J. Recovery and separation of organic acids by membrane-based solvent extraction and pertraction: An overview with a case study on recovery of MPCA. *Sep Purif Technol*. 2005;41:237–266.
3. Lu Y, Chen J. Optimal design of multistage membrane distillation systems for water purification. *Ind Eng Chem Res*. 2011;50:7345–7354.
4. Julianna A F, Sandra E K, Jilska M P, Geoff W S. Poly(tetrafluoroethylene) sputtered polypropylene membranes for carbon dioxide separation in membrane gas absorption. *Ind Eng Chem Res*. 2011;50:4011–4020.
5. Bernardo P, Drioli E, Golemme G. Membrane gas separation: A review/state of the art. *Ind Eng Chem Res*. 2009;48:4638–4663.
6. Jannatduost E, Babaluo A A, Abbasi F, Ardestani M, Peyravi M. Surface modification of nanocomposite ceramic membranes by PDMS for condensable hydrocarbons separation. *Desalination*. 2010;250:1136–1139.
7. Semenova S I. Polymer membranes for hydrocarbon separation and removal. *J Membr Sci*. 2004;231:189–207.
8. Zhang G, Yan H, Ji S, Liu Z. Self-assembly of polyelectrolyte multilayer pervaporation membranes by a dynamic layer-by-layer technique on a hydrolyzed polyacrylonitrile ultrafiltration membrane. *J Membr Sci*. 2007;292:1–8.
9. Yin M, Qian J, An Q, Zhao Q, Gui Z, Li J. Polyelectrolyte layer-by-layer self-assembly at vibration condition and the pervaporation performance of assembly multilayer films in dehydration of isopropanol. *J Membr Sci*. 2010;358:43–50.
10. Toutianoush A, Tieke B. Pervaporation separation of alcohol/water mixtures using self-assembled polyelectrolyte multilayer membranes of high charge density. *Mater Sci. Eng C*. 2002;22:459–463.
11. Ackern F, Krasemann L, Tieke B. Ultrathin membranes for gas separation and pervaporation prepared upon electrostatic self-assembly of polyelectrolytes. *Thin Solid Films*. 1998;327–329:762–766.
12. Li X, Feyter S, Chen D, Aldea S, Vandezande P, Prez F, Vankelecom I. Solvent-resistant nanofiltration membranes based on multilayered polyelectrolyte complexes. *Chem Mater*. 2008;20:3876–3883.
13. Jin W, Toutianoush A, Tieke B. Use of polyelectrolyte layer-by-layer assemblies as nanofiltration and reverse osmosis membranes. *Langmuir*. 2003;19:2550–2553.
14. Saren Q, Qiu C Q, Tang C Y. Synthesis and characterization of novel forward osmosis membranes based on layer-by-layer assembly. *Environ Sci Technol*. 2011;45:5201–5208.
15. Zhang G, Song X, Ji S, Wang N, Liu Z. Self-assembly of inner skin hollow fiber polyelectrolyte multilayer membranes by a dynamic negative pressure layer-by-layer technique. *J Membr Sci*. 2008;325:109–116.
16. Zhang G, Wang N, Song X, Ji S, Liu Z. Preparation of pilot-scale inner skin hollow fiber pervaporation membrane module: effects of dynamic assembly conditions. *J Membr Sci*. 2009;338:43–50.
17. Zhang G, Song X, Li J, Ji S, Liu Z. Single-side hydrolysis of hollow fiber polyacrylonitrile membrane by an interfacial hydrolysis of a solvent-impregnated membrane. *J Membr Sci*. 2010;350:211–216.
18. Wang N, Zhang G, Ji S, Qin Z, Liu Z. The salt-, pH- and oxidant-responsive pervaporation behaviors of weak polyelectrolyte multilayer membranes. *J Membr Sci*. 2010;354:14–22.
19. Jou J, Yoshida W, Cohen Y. A novel ceramic-supported polymer membrane for pervaporation of dilute volatile organic compounds. *J Membr Sci*. 1999;162:269–284.
20. Yoshida W, Cohen Y, Ceramic-supported polymer membranes for pervaporation of binary organic/organic mixtures. *J Membr Sci*. 2003;213:145–157.
21. Xiangli F, Chen Y, Jin W, Xu N. Polydimethylsiloxane (PDMS)/ceramic composite membrane with high flux for pervaporation of ethanol-water mixtures. *Ind Eng Chem. Res*. 2007;46:2224–2230.
22. Chen Y, Xiangli F, Jin W, Xu N. Organic-inorganic composite pervaporation membranes prepared by self-assembly of polyelectrolyte multilayers on macroporous ceramic supports. *J Membr Sci*. 2007;302:78–86.
23. Krajewski S R, Kujawski W, Bukowska M, Picard C, Larbot A. Application of fluoroalkylsilanes (FAS) grafted ceramic membranes in membrane distillation process of NaCl solutions. *J Membr Sci*. 2006;281:253–259.
24. Ismail A F, Kusworo T D, Mustafa A. Enhanced gas permeation performance of poly(ether sulfone) mixed matrix hollow fiber membranes using novel Dynasylan Ameo silane agent. *J Membr Sci*. 2008;319:306–312.
25. Ostwal M, Singh R P, Dec S F, Lusk M T, Way J D. 3-Aminopropyltriethoxysilane functionalized inorganic membranes for high temperature CO_2/N_2 separation. *J Membr Sci*. 2011;369:139–147.
26. Shang L, Jin L, Guo S, Zhai J, Dong S. A facile and controllable strategy to synthesize Au-Ag alloy nanoparticles within polyelectrolyte multilayer nanoreactors upon thermal reduction. *Langmuir*. 2010;26:6713–6719.
27. Harris J J, DeRose P M, Bruening M L. Synthesis of passivating, nylon-like coatings through cross-linking of ultrathin polyelectrolyte films. *J Am Chem Soc*. 1999;121:1978–1979.
28. Moussallem M D, Olenych S G, Scott S L, Keller III T, Schlenoff J B. Smooth muscle cell phenotype modulation and contraction on native and cross-linked polyelectrolyte multilayers. *Biomacromolecules*. 2009;10:3062–3068.
29. Zhang G, Ruan Z, Ji S, Liu Z. Construction of metal-ligand-coordinated multilayers and their selective separation behavior. *Langmuir*. 2010;26:4782–4789.
30. Zhang G, Dai L, Ji S. Dynamic pressure-driven covalent assembly of inner skin hollow fiber multilayer membrane. *AIChE J*. 2011;57:2746–2754.

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