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Integral hollow fiber membrane with chemical cross-linking for pressure retarded osmosis operated in the orientation of active layer facing feed solution

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Abstract

Pressure retarded osmosis (PRO) is an innovative technique to yield osmotic energy. Nevertheless, the PRO performance is exacerbated by the severe membrane fouling occurring within the porous support. It is a potential alternative for sustainable power harvesting to change the membrane orientation from active layer facing draw solution (AL-DS) or PRO mode to active layer facing feed solution (AL-FS) or FO mode for a low-fouling propensity. A novel integral PRO hollow fiber membrane was developed in this work by phase inversion and followed with a facile cross-linking post-treatment. The structure and properties of the resultant membrane were systematically investigated using a series of characterization protocols. The PRO performance of the membrane was studied under various hydraulic pressures at the AL-FS orientation. The results reveal that the substrate with sponge-like structure and relatively dense inner surface can better withstand high pressure in PRO process. Two steps of cross-linking endowed the membrane with a smaller pore size on the outer surface that exhibits high rejection against various inorganic salts. The novel integral membrane can achieve a stable power density output around $4.3 \text{ W}\cdot\text{m}^{-2}$ at 12 ~ 13 bar hydraulic pressure, using a real wastewater reverse osmosis (RO) retentate and 1.0 M sodium chloride as the feed and draw stream, correspondingly. This result demonstrates that the PRO operation in the AL-FS orientation (FO mode) offers a significant advantage over the AL-DS orientation (PRO mode) by eliminating the pretreatment of the feed water or/and other measures associated with membrane fouling control in the PRO mode. To implement the PRO operation with the AL-FS orientation, developing a robust membrane with an integral structure is critical. The newly developed integral hollow fiber membrane via chemical cross-linking presents the potential for PRO operation in the AL-FS orientation.

Keywords:

Pressure retarded osmosis (PRO); integral membrane; low fouling; membrane orientation; chemical cross-linking.

1. Introduction

To meet the increasing global energy demand and challenge of global warming, it is imperative to explore renewable clean energy as an alternative energy resource. The salinity gradient energy produced upon the spontaneous mixing of two different salinity solutions is considered as a viable resource of renewable energy [1, 2]. This form of energy can be harnessed by membrane-based pressure retarded osmosis (PRO) process with no detrimental effects to the environment [3]. In this process, water diffuses through a membrane due to salinity gradient difference between two streams. The osmotic power is then harvested by discharging the pressured inflow stream through a turbine [4, 5].

Over the past five years, several thin-film composite (TFC) membranes with excellent performance were tailored with more desirable structure and permeability properties and applied in PRO process [6-9]. Most recently, PRO research is focused on the energy harvesting using reverse osmosis (RO) retentate from municipal wastewater treatment plants and seawater RO brine as a pair of feed water and draw solution, respectively. This process can convert the two wastes into useful energy with minimized disposal and adverse environmental impacts [10, 11]. Nevertheless, membrane fouling remains one of the main encounters as the porous support is normally placed to face the feed water and is susceptible to fouling. In particular, the feed water from municipal wastewater process normally contains high amounts of organic, inorganic foulants and microbial species [12-14]. The foulants can penetrate the porous substrate and get stuck beneath the dense selective layer where the cross-flow induced hydrodynamic shear force is inefficient for the removal of the trapped foulants, resulting in a severe reduction of water flux [15, 16]. Many efforts have been conducted to alleviate fouling in the PRO process including the surface modification on the substrate [17-19], the fabrication of double-skinned membrane [20] and the employment of pretreatment

process [13, 21]. Nevertheless, these approaches only illustrated improved PRO performance at lab scale, and their applicability in large-scale PRO needs to have further evaluation. For instance, the modification methods for fabricating antifouling membranes are usually complicated with strict reaction conditions and difficult for scaling up; some solvents involved are environmental unfriendly [17, 20]. In addition, the increased energy and chemical consumptions, as well as high operating expenses caused by the pretreatment processes, are also a big concern [3].

Since the membrane fouling occurring within the substrate is the major barrier for PRO power generation, it may benefit the production of consistent power density by switching the membrane orientation from the conventional active layer facing draw solution (AL-DS) or PRO mode to active layer facing feed solution (AL-FS) or FO mode owing to the low membrane fouling tendency [14, 15, 22]. Besides, the external fouling occurred on the top of the selective layer is more reversible and easily removed by flushing [23-26]. Kim's study also shows that for high fouling feed water, it is more economically feasible to operate PRO in the FO mode rather than in the other orientation attributed to alleviated membrane fouling that reduces the energy and expenses mandatory for pretreatment and backwash [27]. She et al. observed stable water flux using CTA membrane in AL-FS orientation using wastewater retentate as feed solution compared to that in the AL-DS orientation, demonstrating the advantage of AL-FS orientation in a severe fouling environment and the mechanical stability of integral membrane in this orientation [28]. These research works have called on future endeavors on the development of high performance integral membranes for PRO process.

It was noted that most of the present PRO membranes reported are thin film composite (TFC) membranes with good mechanical stability in PRO operation in the AL–DS orientation [22, 29]. However, when the hydraulic pressure is applied to the porous substrate, the thin film polyamide selective layer tended to be damaged or even detached from the surface even under a low pressure [28, 30]. In the AL-FS orientation, the pressure is applied on the back side of the thin selective layer (100-300 nm) through the porous substrate and pressurized the thin film unevenly to destruct its integrity [28]. On the other hand, the flat-sheet integral CTA membrane could withstand the high pressure in the AL–FS orientation because of its integral structure, but CTA membrane usually suffers poor chemical and biological stability as compared to other membrane materials [31]. Also, in some ways the performance of flat-sheet membranes depends on spacers used in the feed channel [22]. The possible adverse effects induced by spacers used should be considered in real applications [32, 33]. In contrast, the hollow fiber membranes with self-supported structures would be a promising alternative since no spacer is needed [34, 35]. Thus, it is imperative to develop mechanically robust hollow fiber membrane with desirable transports properties for PRO operation in the FO mode.

The objective of this study is to develop an integral PRO hollow fiber membrane suitable for running in the AL–FS orientation under high pressure for osmotic energy harvesting. Polyamide-imide (PAI) was selected as the polymeric material for preparing the substrate, not only because its outstanding mechanical property and chemical stability which make it a good candidate for mechanically robust PRO membrane, but also because it can be easily modified for diverse applications through functionalization of imide groups [36, 37]. The integral PAI PRO hollow fiber membranes were synthesized by performing the phase inversion, followed by a facile and scalable cross-linking post-treatment method using

environmentally friendly solvents. The membranes were characterized thoroughly using a wide range of standard protocols. The PRO performances of the membranes in the FO mode using a real wastewater RO retentate as the feed were subsequently evaluated. This study is believed to be the first attempt to fabricate integral PAI hollow fiber membranes with facile post-treatment for PRO application in the AL-FS orientation. It is expected to provide new perspectives for fouling control so that the feed pretreatment and other measures associated with fouling can be eliminated for a sustainable PRO operation.

2. Experimental

2.1 Materials

Torlon® 4000T-MV (Polyamide-imide PAI, Solvay Advanced Polymers) and *N*-Methyl-2-pyrrolidone (NMP, >99.5%, Merck Millipore) were adopted for developing the hollow fiber support. Poly (allylamine hydrochloride) (PAH, Molecular Weight 450,000 g mol⁻¹) and glutaraldehyde (GA, 50 wt.% in H₂O) (Sigma-Aldrich) were adopted as cross-linking agents. Dextran with various molecular weights (M_w) (6000–500,000 Da) provided by Sigma-Aldrich was adopted to characterize the molecular weight cut-off (MWCO) of membrane substrates. Sodium chloride (NaCl), sodium sulfate (Na₂SO₄), magnesium sulfate (MgSO₄) and magnesium chloride (MgCl₂) were purchased from Merck Millipore and used for testing salt rejections of membranes. Chemicals were analytical grade and employed as received. Deionized (DI) water was provided by the Milli-Q® water purification system (Merck Millipore).

2.2 Fabrication of polyamide-imide supports

Hollow fiber substrates were produced using a dry/jet wet phase inversion spinning technique. The detailed fabrication methods were reported elsewhere [38, 39]. Briefly, polyamide-imide powder and additives were dissolved in an NMP solution after removing moisture in the PAI at 50 °C over one day. The dope was continuously stirred at 60 °C for three days until the solution becomes homogeneous. The spinning conditions were listed in Table 1. Two different substrates, fabricated by controlling the bore fluid compositions, were denoted as ST#1 and ST#2.

Table 1 Dope composition and spinning conditions

Substrate code	ST#1	ST#2
Dope composition (PAI/PEG200/H ₂ O/NMP) (wt. %)	22/22.5/0.1/53.4	
Dope rate (mL/min)	2.4	
Internal coagulant composition NMP/H ₂ O (vol. %)	90/10	50/50
Internal coagulant rate (mL/min)	1.2	
Gap distance (cm)	0.5	
Winding speed (m/min)	18.8	
Ambient temperature (°C)	23 ± 1	
Coagulation bath temperature (°C)	23 ± 1	
Humidity (%)	75-80	
Spinneret size (mm)	ID/OD = 0.5/1.0	

2.3 Fabrication of integral PRO hollow fiber membrane by chemical cross-linking

The chemical cross-linking post-treatment was performed via soaking the substrates into a 0.06 mol·L⁻¹ PAH solution (a blend of 2-propanol and water: 50/50 vol. %, pH adjusted to 10) at a temperature of 70 °C for one hour followed by thoroughly rinsing using DI water to remove the unreacted chemicals. The resultant PAH cross-linked membranes were denoted as ST#X-PAH (X represents substrate number). To further improve membrane performance, the ST#X-PAH membrane was further cross-linked using 0.5wt. % GA solution for 30 minutes and the resultant membranes were denoted as ST#X-PAH/GA.

2.4 Membrane characterization and performance assessment

2.4.1 The characterization of membrane morphology and surface chemistry

The fibers before and after post-treatment were characterized using field emission scanning electron microscope (FESEM JSM-7200F, JEOL, Japan). Information about surface functional groups of the membranes before and after the modification was obtained by using via attenuated total reflection-fourier transforms infrared spectroscopy (ATR-FTIR) (IR-Prestige-21, Shimadzu, Japan). The surface chemistry of the membranes was performed within the range from 650 to 4000 cm^{-1} . The surface zeta potentials of the fibers were tested using an electrokinetic analyzer (SurPASS^{TM}, Anton Paar GmbH, Austria) using a 10 mM NaCl background electrolyte solution in the pH range of 3–9. Automatic titration was conducted with 0.05 M HCl and 0.1 M NaOH solutions to adjust the pH. The surface charge results were obtained using Helmholtz-Smoluchowski equation [38, 40]. The mechanical properties of the membranes were evaluated via tensile modulus and burst pressure. A Zwick 0.5 kN testing machine was adopted to determine the tensile modulus. The specific testing method of burst pressure was similar to our previous study [7].

2.4.2 Measurements of the intrinsic properties of PAI substrates

To test membrane separation performance, each hollow fiber module was made using fifteen hollow fibers in a Teflon tubing in 22 cm effective length. The pure water permeability (PWP) and MWCO of PAI substrates were tested on a cross-flow filtration system at 1 bar. For the PWP test, membrane modules were pressured for one hour with Milli-Q water circulated through the outer surface of fibers at a 0.11 $\text{m}\cdot\text{s}^{-1}$ cross-flow velocity prior to permeate sample collection. The PWP can be determined using Eq. (1):

$$\text{PWP} = \frac{Q}{\Delta P \times A_m} \quad (1)$$

where Q is the volumetric rate of the permeate collected ($\text{L} \cdot \text{h}^{-1}$), A_m is the membrane area (m^2), and ΔP is the applied pressure (bar).

A $2 \text{ g} \cdot \text{L}^{-1}$ mixed dextran solution (Mw ranges from 6,000 to 500,000 Da) was adopted as feed to test the MWCO of the substrates. The dextran concentrations were analyzed by gel permeation chromatography (GPC) (PL-GPC 50 plus system). The detailed method was described previously [7].

2.4.3 Measurement of intrinsic properties of cross-linking modified membranes

The properties of the modified membranes were determined using the above-mentioned filtration system at 2 bar. The water permeability coefficient (A value) of the cross-linked membrane was measured with deionized water as the feed stream, and the rejections to different inorganic salts were determined using 500 mg L^{-1} NaCl, MgCl_2 , Na_2SO_4 and MgSO_4 single salt as feed, respectively. The solute rejections were determined by the conductivity difference in feed solution and permeate. The MWCO of the cross-linking modified membranes were estimated using a series of neutral solutes, including glycerol, ribose, and glucose. A total organic carbon analyzer was used to examine their concentrations (TOC-VCSH, Shimadzu, Japan). All these feed solutions were pumped through the outer skin of the membranes with a $0.18 \text{ m} \cdot \text{s}^{-1}$ cross-flow velocity.

2.4.4 PRO performance evaluation

The PRO performances of membranes after post treatment were evaluated via a PRO system which has been reported in our previous studies [7, 41]. The AL-FS orientation was chosen for all PRO tests throughout our study, and the solute rejection skin is on the shell side of the membranes. A 1.0 M magnesium chloride or sodium chloride was employed as the draw stream and driven through the lumen surface of the fibers at different pressures ranging from 0 to 18 bar. The solute concentration in the draw stream was reserved constant by continuously dosing a highly-concentrated salt solution. A variable-speed peristaltic pump was used to drive the feed streams through the shell side of the fibers, and its volume was also kept constant by dosing feed water during the experiments. The flow rates of the feed and draw streams were $1 \text{ L} \cdot \text{min}^{-1}$ and $0.15 \text{ L} \cdot \text{min}^{-1}$, correspondingly. The temperature was $23 \pm 1^\circ\text{C}$. The performance was tested in triplicate with fresh hollow fiber modules, and the average value was presented.

The water flux (J_w) through the selective layer of the membrane was calculated by the Eq. (2):

$$J_w = \frac{\Delta V}{A_m \Delta t} \quad (2)$$

where ΔV (L) is the volume difference of the dosing feed, Δt (h) is time interval.

The salt flux (J_s) in the feed water, given by:

$$J_s = \frac{\Delta(C_{fe} V_f)}{A_m \Delta t} \quad (3)$$

where C_{fe} is the solute concentration and V_f is the volume of the feed stream. The power density (W) was obtained from Eq. (4):

$$W = J_w \Delta P \quad (4)$$

To evaluate the low fouling properties of the integral membrane in the AL–FS orientation, a wastewater reverse osmosis retentate from a local municipal wastewater treatment plant was applied as the feed, while NaCl was adopted as the solute for draw stream (1.0 M). Prior to fouling experiments, baseline test was conducted using deionized water as feed at 12-13 bar for 300 minutes. After that, the feed solution was changed to the wastewater RO retentate, and the experiment was conducted continually at 12-13 bar for 300 minutes.

3. Results and discussion

3.1 Fabrication of PRO membrane by PAH cross-linking modification

3.1.1 Characteristics of polyamide-imide substrate

The resultant supports were characterized using FE-SEM, and the images are shown in Fig. 1. For the two substrates ST#1 and ST#2, the dope composition and spinning conditions were kept the same except for the bore fluid composition used. By adjusting the bore fluid solution, the lumen side surface and cross-section pore structures of the two substrates are rather different. It is observed from Fig. 1 (a1 and b1) that the finger-like structure was developed beneath the inner surface of ST#1, while the ST#2 presented a sponge-like framework with several macrovoids in the middle. The finger-like structure is probably better for mitigating the internal concentration polarization (ICP) effect and increasing water permeability, while the sponge-like structure is believed to provide better mechanical stability [41, 42]. As shown in Fig. 1 (a2 and b2), the more dense sponge-like pore structure beneath the inner surface of the ST#2 membrane makes it possible to better withstand the high pressure as compared to the ST#1 membrane. From the surface images Fig. 1 (a3, b3, and a4, b4), abundant pores are

observed on the inner surface of both substrates, while almost no pore is observed on the shell surface, indicating the more dense skins formed on the outer surface of the fibers.

The properties of the two polyamide-imide substrates are listed in Table 2. The hollow fiber substrates are designed to possess relatively smaller dimensions (inner diameter/outer diameter, ID/OD, around 0.4/0.7 mm/mm), which are favorable to membrane mechanical properties [41]. The ST#1 membrane has slightly higher PWP than the ST#2 membrane, probably ascribing to the finger-like structure and very large pores on the inner surface. The MWCO values of both substrates tested from the shell side are relatively small, which is favorable for the subsequent chemical post-treatment to further decrease the pore size and form the solute rejection layer on the outer surface. The two PAI substrates possess high rigidity with a tensile modulus of 215–244 MPa, which are comparable with our previous polyetherimide (PEI) hollow fiber membranes [7, 41]. In comparison with the ST#1 membrane, the tensile modulus of the ST#2 membrane is slightly higher due to its more uniform distribution of the tension in the sponge-like structure [41]. The two substrates have similar burst pressures of up to 22 bar.

Fig. 1. FESEM images of PAI supports: (a1 and b1) cross section of ST# 1 and ST#2; (a2 and b2) cross-section adjacent to the inner area of ST#1 and ST#2; (a3 and b3) inner area of ST#1 and ST#2; (a4 and b4) outer skin of ST# 1 and ST#2.

Table 2 Properties of the PAI substrates

Substrate	Dimensions (μm)			PWP ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	MWCO (kDa) ^a	Tensile modulus (MPa)	Burst pressure (bar)
	ID	OD	Thickness				
ST# 1	401 ± 6	666 ± 6	132 ± 5	106 ± 10	6	215 ± 4	21 ± 2
ST# 2	432 ± 6	675 ± 11	121 ± 3	91 ± 8	19	244 ± 6	22 ± 2

^a Dextran filtration was conducted by circulating the dextran from shell side of the fiber

3.1.2 Characteristics of PAH cross-linked hollow fiber membranes

Fig. 2 shows the morphologies of the PAH cross-linking modified hollow fiber membranes ST#1–PAH and ST#2–PAH. Compared with the original substrates, the pore structures of the membrane surface do not change much after modification as shown in Fig.2 (a1, b1 and a2, b2). There is no skin layer formed on the inner surface after modification, but small nodules are observed on both inner and outer surfaces. After the PAH post-treatment, suggesting the success of cross-linking reaction. Similar findings have been reported in the recent publication, where the reaction between P84 polyimide membrane and polyethyleneimine was investigated [43]. During the PAH cross-linking reaction, PAH molecules may be able to diffuse into the hollow fiber substrates from both lumen and shell sides. The PAH molecules could gradually anchor onto pore wall and seal the pore, leading to the diminution of the outer skin pore size and the increase in filtration resistance [44]. As shown in Fig. 2(a3) and

(b3), the cross-section adjacent to the outer skin of the modified membranes presents a dense selective skin on top of the support layer.

Fig. 2. FESEM images of the inner area morphologies (a1 and b1), outer skin morphologies (a2 and b2), and cross-section morphologies adjacent to the outer surface (a3 and b3) of the PAH cross-linked membranes ST#1-PAH (a series) and ST#2-PAH (b series).

The intrinsic properties of the ST#1-PAH and ST#2-PAH are summarized in Table 3. The water permeability (A value) and solute rejections were estimated using a cross-flow reverse osmosis system at 2 bar, while the structure parameters (S values) were evaluated using water flux tested in forward osmosis (FO) tests. The A value of the ST#1-PAH and ST#2-PAH membranes are 1.98 and $1.14 \text{ L} \cdot \text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, respectively. The possible reason for the lower A value of the ST#2-PAH membrane is that its sponge-like structure and smaller inner surface pores increase mass transfer resistance as compared to the finger-like structure and very large inner surface pores of the ST#1-PAH membrane [45]. The rejections to 500 ppm NaCl and MgCl_2 of these two membranes are similar, around 70% and 92%, respectively. After the PAH cross-linking, an NF-like solute separation skin was developed on the shell area of fibers. Since the MgCl_2 rejections of the membranes are relatively high, MgCl_2 was selected as the draw solution for evaluating the performance with the selective layer facing

feed streams, which will be discussed in the following section. As listed in Table 3, the tensile modulus of the fibers is not affected much by the cross-linking reaction.

Table 3 Intrinsic properties of PAH cross-linked hollow fiber membranes

Membranes	Water permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \text{bar}^{-1}$)	NaCl rejection ^a (%)	MgCl ₂ rejection ^a (%)	Structural parameter ^b (μm)	Tensile modulus (Mpa)
ST# 1-PAH	2.0 ± 0.3	72 ± 4	92 ± 3	621	207 ± 1
ST# 2-PAH	1.1 ± 0.2	69 ± 5	93 ± 1	437	243 ± 5

^a Salt rejections were tested using 500 ppm NaCl and MgCl₂ as feed at 2 bar, respectively.

^b The membrane structure parameter was calculated based on the methods reported in our previous publications [9, 24].

3.1.3 PRO performance of PAH cross-linked membrane

The PRO performances of the integral membranes were evaluated with deionized water and MgCl₂ (1.0 M) as feed and draw, correspondingly. Various hydraulic pressures were applied in the draw, and the experiment results for membrane performance are presented in Fig. 3. It is indicated in Fig. 3 (a) that the water flux (J_w) of the ST#1-PAH and ST#2-PAH membranes tested at a pressure of 0.4 bar are 20.5 and 26.9 $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, correspondingly. In the PRO process, the water flux is determined by the membrane intrinsic properties (A value and B value) and structural parameter S value of the membrane as well as the operation conditions. While the A value of the ST#2-PAH is smaller than that of the ST#1-PAH, the lower S value of the ST#2-PAH membrane is useful in mitigating the dilutive ICP effect, leading to a higher water flux than the ST#1-PAH membrane [27]. As shown in Fig. 3 (a), with the pressure increase from 0 – 18 bar, the PRO water flux of both membranes decreases gradually due to the decline of driving force. The specific salt flux (J_s/J_w) is the indicator in the osmotically driven membrane processes for revealing the reverse salt diffusion.

Minimizing the reverse salt diffusion could reduce ICP effect and mitigate membrane fouling [46]. As shown in Fig. 3(b), the J_s/J_w of the ST#2–PAH membrane shows relatively stable over the entire operating pressure, while the J_s/J_w of the ST#1–PAH membrane increases obviously with the rise in applied pressure. This suggests the ST#1–PAH membrane suffers severe salt leakage or deformation under high pressures. Fig. 3(c) reveals that the ST#2–PAH membrane harvests a maximum power density of $6.5 \text{ W}\cdot\text{m}^{-2}$ at the hydraulic pressure of 15 bar while the power density of ST#1–PAH membrane reaches a peak value of around $3.3 \text{ W}\cdot\text{m}^{-2}$ at the pressure of 10 bar. As observed from FESEM characterization, the sponge-like structure and smaller inner surface pores of the support makes the ST#2–PAH membrane a good candidate for PRO application. From the above discussion, the ST#2–PAH membrane has better mechanical stability under high-pressure operation and higher power density output, and thus it is chosen for further study.

Fig. 3. PRO performance of the PAH cross-linked hollow membranes at different operating pressures: (a) the water flux J_w , (b) the specific salt flux (J_s/J_w), (c) the power density W . Testing conditions: deionized water and 1M MgCl₂ as the feed and draw stream, respectively.

3.2 Fabrication of PRO membrane by PAH cross-linking followed by GA cross-linking

In real PRO application, seawater or seawater desalination brine is usually used as the draw solution, in which NaCl is the main solute. Therefore, the selectivity of NaCl of PAH cross-linked membrane needs to be further improved for its potential application in PRO process. In order to improve the NaCl rejection, GA was adopted to conduct the second step of cross-linking on the ST#2-PAH membrane and the resultant membrane is denoted as ST#2-PAH/GA.

3.2.1 Characterizations of PAH/GA cross-linked hollow fiber membrane

The surface and cross-section morphologies of the ST#2-PAH/GA membrane were not changed compared to the ST#2-PAH membrane, and thus the relevant FESEM images are not shown here.

The possible cross-linking reactions between PAI substrate and PAH/GA are illustrated in Fig. 4 and verified by the ATR-FTIR characterization as shown in Fig.5. The imide rings in PAI were opened, and the amine groups from PAH were covalently bonded onto the PAI. After that, the free amine groups in PAH can be further covalently bonded with aldehyde groups from GA. As depicted in Fig. 5, a few characteristic peaks for the imide function group including 1778, 1719, 1379, 1109 and 725 cm^{-1} are observed for the PAI substrate [47, 48]. The imide peaks were observed to become weakened after the cross-linking post treatment using PAH due to the formation of a covalent bond between amine groups and imide rings [49].

Fig. 4. Possible mechanism of chemical reaction between polyamide-imide and PAH/GA

Fig. 5. ATR-FTIR spectra of the support fiber before and after modification

The surface charge of the pristine membranes and those after modification were investigated using streaming potential measurement at pH 4–9 and the results are presented in Fig. 6. It presents that PAI hollow fiber substrate is negatively charged throughout the entire testing pH range. After PAH cross-linking, the membrane surface becomes positively charged below the pH of 8.6 (isoelectric point) attributed to the protonation of amine groups imparted by PAH grafting. However, further introducing of GA consumes partial amine groups on PAH cross-linked membrane, lowering the positive charge.

Fig. 6. Surface zeta-potential of the substrate and modified membranes.

3.2.2 Intrinsic properties of PAH/GA cross-linked hollow fiber membrane

The intrinsic permeation properties of the ST#2–PAH/GA membrane including A value, B value, and NaCl rejection are summarized in Table 4. The A value of the membrane decreases to $0.66 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ while the sodium chloride rejection increases to 80.1 % after the GA modification. The reaction between GA and amine functional groups on the substrate after the PAH cross-linking would be able to further seal the membrane pores, leading to a rise in filtration resistance and a decline in pore size of rejection layer.

Table 4 Intrinsic properties of the ST#2–PAH/GA hollow fiber membrane

Membrane	A ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)	B ($\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	NaCl rejection ^a (%)
ST#2–PAH/GA	0.66 ± 0.09	0.32 ± 0.03	80 ± 2

^a Salt rejections were tested using 500 ppm NaCl as feed

The rejections to the neutral solutes with different molecular weights were measured to estimate the MWCO of the modified membranes. Table 5 lists the properties of these neutral solutes, and their rejections by the PAH cross-linked, and PAH/GA cross-linked membranes. The MWCO of the membranes can be examined by plotting the rejection of the solutes against their molecular weights. The MWCO of the ST#2-PAH and ST#2-PAH/GA membranes are 143 Da and 127 Da, respectively. This indicates that the selective layer is further tightened after the GA cross-linking.

Table 5 Properties and rejections of the neutral solutes ^a

Solute	M_w (Da)	Stocks radius (nm)	ST#2-PAH rejection ^a (%)	ST#2-PAH/GA Rejection ^a (%)
Glycerol	92	0.26	59	81
Ribose	150	0.31	95	96
Glucose	180	0.35	97	97

^a The solute rejection was tested using 200ppm feed solutions at 2 bar.

The rejections of the modified membranes against different inorganic salts were determined by performing the filtration test with 500 ppm NaCl, MgCl₂, Na₂SO₄, and MgSO₄ single salt as feed, respectively. It is observed in Fig. 7 that the PAH cross-linked membrane shows 68% rejection to NaCl and more than 93% rejections against MgCl₂, Na₂SO₄, and MgSO₄, which suggests the size exclusion plays a significant role [50]. After GA cross-linking, the NaCl rejection increases to 80.1% while the MgCl₂ rejection slightly decreases to 87.4%, which may be due to the change of surface charge property as shown in Fig. 6. The membrane surface became more negatively charged after GA crosslinking, leading to a lower rejection towards Mg²⁺ due to the Donnan exclusion mechanism [51].

Fig. 7. Separation performances of the PAH and PAH/GA cross-linked hollow fiber membranes. Experiments were conducted at 2 bar using 500 ppm single salt solution.

3.2.3 PRO performance of the ST#2-PAH/GA membrane

The PRO performance of the ST#2-PAH/GA membrane was investigated in the AL-FS orientation with deionized water and NaCl (1.0 M) as feed and draw stream, respectively. The experiment results for J_w , J_s/J_w , and W of the ST#2-PAH/GA membranes are presented in Fig. 8. The J_w declines gradually with the escalation in the operating pressure. The specific salt flux J_s/J_w keeps constant at lower trans-membrane pressure (< 12 bar) and slowly increases with the increase of pressure from 12 to 16 bar. It produces a maximum power density around $5.1 \text{ W} \cdot \text{m}^{-2}$ at the pressure of 16 bar. This result shows the potential of the PAH/GA cross-linked hollow fiber membrane for the PRO application under the AL-FS orientation. Then, the newly developed PRO membrane with high durability was examined using a real wastewater RO retentate as feed, which will be discussed in the following section.

Fig. 8. PRO performance of the ST#2-PAH/GA membrane at various operating pressures: (a) J_w , (b) J_s/J_w , (c) W . Testing conditions: Milli-Q water (feed) and 1.0 M NaCl (draw) at ambient temperature.

3.3 PRO performance using real wastewater RO retentate as feed

The wastewater RO retentate, containing various inorganic and organic foulants, is from a local municipal wastewater RO plant in Singapore. The detailed composition can be referred to our previous work [28, 52]. The fouling behavior of the PAH/GA cross-linked membrane was evaluated in the AL-FS orientation in PRO process. Before conducting the fouling test, deionized water was adopted as a feed for benchmarking. As illustrated in Fig. 9, the average power density of the ST#2-PAH/GA membrane is $4.8 \text{ W}\cdot\text{m}^{-2}$ with deionized water as the feed stream for 300 min continuously operation at a 12~13 bar hydraulic pressure. After changing the feed to wastewater RO retentate, the power density slightly decreases and maintains constant at around $4.3 \text{ W}\cdot\text{m}^{-2}$. The slight decrease of the power density might be owing to the increase in osmotic pressure in the feed (the conductivity of wastewater RO retentate is around $2.4 \text{ mS}\cdot\text{cm}^{-1}$) as compared to the benchmark. The power density of the newly developed membrane keeps constant during the entire experiment, indicating its advantages of lower membrane fouling tendency when operated with selective skin facing the feed streams. The results reveal that this novel PAH/GA cross-linked integral membrane is promising for fouling control in PRO process. After further crosslinked using GA solution, the resulted membrane has a negative charge when pH above 4 (Fig. 6), which may also contribute to its antifouling properties due to the fact that most organic foulants are negatively charged. Since TFC membranes can only be applicable under the AL-DS orientation (In AL-FS orientation, the thin film selective layer would be deteriorated or even detached from surface even under low pressure [30]), this cross-linking method provides an alternative approach to fabricate robust membranes to run in the FO mode in PRO process to resist fouling and maintain stable performance.

Fig. 9. The power density of the ST#2-PAH/GA membrane with the operation time. The experiment was conducted with Milli-Q water as the feed and sodium chloride (1.0 M) as the draw stream for the baseline test while wastewater RO retentate as the feed for fouling test at 12~13 bar hydraulic pressure.

3.4 Performance comparison to other membranes that reported in the literature study

The intrinsic PRO performances tested in the AL – FS orientation of the novel integral hollow fiber membranes together with the membranes reported in literature are summarized in Table 6, while their fouling performances using the real wastewater retentate as feed were compared in Table 7. It can be seen that the cross-linking modified integral hollow fiber membranes developed in the current study present better performance as compared to those reported integral CTA membranes. A peak power density of $5.1 \text{ W} \cdot \text{m}^{-2}$ can be achieved using deionized water as feed and sodium chloride (1.0 M) as draw streams in the AL – FS orientation as listed in Table 6. When using the real wastewater retentate as feed, the newly developed integral membrane showed a very stable performance with a power density of $4.3 \text{ W} \cdot \text{m}^{-2}$ for 300 min operation at 13 bar, which is higher than that of the CTA membrane.

The results demonstrate the great potential of PAH/GA cross-linked hollow fiber membrane for PRO application. Further investigation is required to improve the performance of PAH/GA membranes, including optimizing the membrane structure to decrease S value and increase water permeability, and further enhancing the mechanical strength of the membranes to withstand higher pressures and thus produce a higher power density.

Table 6 Summary of PRO performance of membranes tested in AL-FS orientation

Membrane	Feed solution	Draw solution	J_w @ 0 bar ($\text{L}\cdot\text{m}^{-2}\text{h}^{-1}$)	Peak Power density ($\text{W}\cdot\text{m}^{-2}$)	J_s/J_w @ peak power density ($\text{mol}\cdot\text{L}^{-1}$)	Collapse pressure (bar)	Orientation	Reference
ST#2-PAH	DI water	1.0 M MgCl_2	27.0	6.5	0.09	>18	AL-FS	Current work
ST#2-PAH/GA	DI water	1.0 M NaCl	20.0	5.1	0.16	>16	AL-FS	Current work
HTI-CTA	DI water	0.5 M NaCl	7.8 ^a	0.8 ^a	/	>15	AL-FS	[27]
HTI-CTA	DI water	1.0 M NaCl	10.1 ^a	2.3 ^a	/	>15	AL-FS	[27]

^aReadings from figures

Table 7 Comparison of power density of PRO membranes tested in the AL-FS orientation using wastewater RO retentate as feed

Membrane	DS	Feed	Initial W ($\text{W}\cdot\text{m}^{-2}$)	Final W ($\text{W}\cdot\text{m}^{-2}$)	Applied Pressure (bar)	Orientation	Reference
ST#2-PAH/GA	1 M NaCl	Wastewater retentate	4.3	4.3 @ 300 mins	13	AL-FS	Current work
HTI-CTA	1 M NaCl	Wastewater retentate	2.8 ^a	2.8 ^a @ 240 mins	10	AL-FS	[28]

^aReadings from figures

4. Conclusions

In this study, an innovative integral hollow fiber membrane was developed by employing a facile cross-linking method for PRO application in the unconventional orientation (selective layer facing the feed streams). The structure and properties of the newly developed membranes have been characterized thoroughly, and the performance in PRO operation was subsequently investigated. The viability of PRO operation in the unconventional orientation for power generation was also assessed using a real wastewater RO retentate as feed. The major results of the work are summarized as follows:

- (1) Two hollow fiber substrates with different pore structures were fabricated to investigate the proper structure of the integral membrane that could be operated in the selective layer facing feed orientation. The sponge-like structure with a selective layer on the outer surface and smaller inner surface pore are more suitable for PRO operation than in AL-FS orientation. The ST#2-PAH membrane can endure the high pressure from the lumen surface and a peak power density of $6.5 \text{ W}\cdot\text{m}^{-2}$ can be achieved at the pressure of 15 bar with pure water as the feed and MgCl_2 (1.0 M) as the draw streams in the AL-FS orientation.
- (2) The PAH/GA cross-linked membrane shows high rejections against each of 500 ppm inorganic salt MgCl_2 , Na_2SO_4 and MgSO_4 under 2 bar. It presents an MWCO of 127 Da and 80% rejection to 500 ppm NaCl. The maximum power density can reach $5.1 \text{ W}\cdot\text{m}^{-2}$ at 16 bar in the AL-FS orientation with deionized water and 1.0 M sodium chloride as feed and draw, correspondingly.
- (3) By adopting wastewater retentate as the feed solution, the integral ST#2-PAH/GA membrane illustrates superior antifouling performance while the power density keeps constant at around $4.3 \text{ W}\cdot\text{m}^{-2}$ at 12~13 bar using 1.0 M sodium chloride as the draw stream (equivalent to seawater brine) during the entire experiment of 300 minutes.

These results demonstrate the advantages of the AL–FS orientation for alleviating membrane fouling in osmotic power generation process and indicate the great potential of the mechanically robust PAH/GA cross-linked hollow fiber membrane for osmotic energy harvesting.

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