Synthesis of high flux forward osmosis membranes by chemically crosslinked layer-by-layer polyelectrolytes

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ARTICLE INFO

ABSTRACT

Forward osmosis (FO) membranes were successfully fabricated using layer-by-layer (LbL) assembly of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene-sulfonate) (PSS) on a porous polyacrylonitrile (PAN) substrate. In addition, chemical crosslinking of LbL polyelectrolyte layers was performed with glutaraldehyde (GA). The resultant crosslinked (the xLbL series) and non-crosslinked (the LbL series) membranes were characterized in terms of the substrate morphology and structure, the separation layer water permeability and salt rejection, and the FO water flux and solute flux performance. Both LbL and xLbL membranes had relatively high water permeability ($\sim$ or >7.0 L/m^2 h bar). On the other hand, the crosslinked xLbL membranes showed better and more stable MgCl$_2$ rejection, leading to a relatively low FO solute reverse transport (the solute flux over water flux ratio < 6 mM regardless of draw solution (DS) concentration and membrane orientation). High FO water fluxes were achieved for both crosslinked and non-crosslinked membranes, where a thin substrate with finger-like pores were adopted to minimize internal concentration polarization in the porous support layer. The crosslinked membrane xLbL3 (with 3 PAH/PSS deposition layers) had an FO water flux of $\sim$100 L/m^2 h in the active-layer-facing-DS orientation using a 2 or 3 M MgCl$_2$ draw solution and distilled water as the feed water, which clearly demonstrates the potential of LbL membranes for high flux FO applications.

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1. Introduction

Forward osmosis (FO) has attracted significant attention in recent years as a potential low-energy-consumption alternative process to conventional pressure-driven membrane processes, with possible applications in wastewater treatment [1–4], water purification [5,6], seawater desalination [7–9], food processing [10,11], valuable product concentration [11,12], and osmotic power generation (using a derivative pressure retarded osmosis process [13–17]). The FO process utilizes the osmotic pressure difference across a semi-permeable membrane to drive water from a low-osmotic-pressure feed solution (FS) to a high-osmotic-pressure draw solution (DS), during which no externally applied hydraulic pressure is required [18]. Existing literature also shows that FO tends to have lower fouling propensity compared to reverse osmosis (RO) [19–22], although the mechanisms involved in FO fouling tends to be more complicated compared to RO fouling [12,22–24].

In a recent review on FO [18], the need for developing high performance FO membranes is highlighted. Conventional RO membranes do not perform well in FO testing mode as a result of severe internal concentration polarization (ICP) of solutes inside their porous support layers [14,22,25–27]. As revealed by a number of modeling studies as well as experimental investigations [14,22,25–31], ICP significantly reduces the available osmotic pressure difference across the active rejection layer, and thus it poses a severe limit on the available FO water flux. It is generally agreed among the FO researchers that a high-flux FO membrane requires (1) an active rejection layer with high water permeability to reduce the membrane frictional resistance loss and (2) a support layer with a small structural parameter S (i.e., substrate thickness × tortuosity/porosity) to control ICP [22,25–32]. The early generation of FO membranes was based on asymmetric dense membranes prepared by phase inversion [33,34]. While these types of membranes can have reasonably low S values, their water permeability is typically limited. For example, the commercial FO membranes developed by Hydration Technology Inc. (HTI) have water permeability values $A \sim$ or <1 L/m^2 h bar [27]. As a result, the corresponding FO water flux was still relatively low ($\sim$9 L/m^2 h in the active layer facing feed solution orientation (AL-FS) using 0.5 M NaCl as DS and 10 mM as FS for the Hydrowell membrane [22,27]). A significant recent advancement was the development of thin film

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composite (TFC) FO membranes [27,32,35–37]. With similar S values but significantly higher water permeability ($A > 1$ L/m^2 h bar), these TFC FO membranes were able to achieve water fluxes twice as high as that of commercial HTI membranes under similar testing conditions (e.g., 0.5 M NaCl as DS in AL-FS orientation) [32], which clearly demonstrates the importance of the rejection layer water permeability in FO applications.

The layer-by-layer (LbL) assembly method may provide an alternative way for synthesizing high performance FO membranes [38]. LbL assembly is a versatile method for creating ultra-thin barrier layers assembled by oppositely charged polyelectrolytes [39,40]. It has been applied to fabricate various types of membranes such as nanofiltration (NF) and pervaporation membranes with high permeability and good selectivity [40–42], although large scale production of these membranes is still limited due to the relatively high production cost [40]. LbL membranes have high thermal stability and good solvent resistance [39–41]. The pH stability and long-term stability can be improved by performing crosslinking treatment [43]. We have recently developed high-water-permeability LbL FO membranes ($A > 7$ L/m^2 h bar) [38]. Such LbL membranes showed remarkable FO performance (e.g., 15 L/m^2 h in AL-FS using a DS of only 0.1 M MgCl$_2$). Unfortunately, the rejection of these membranes decreased dramatically when the active layers were exposed to an high ionic strength environment (e.g., in the active layer facing the DS (AL-DS) orientation) due to the suppression of the Donnan exclusion effect [38].

The objectives of the current study was to develop chemically crosslinked LbL (xLbL) FO membranes with improved rejection properties. To the best knowledge of the authors, this is the first investigation on the fabrication and characterization of xLbL FO membranes. For the first time, the current study demonstrated superior FO water flux > 100 L/m^2 h with stable solute rejection for xLbL membranes (e.g., by using a 3.0 M MgCl$_2$ DS).

2. Experimental

2.1. Materials and chemicals

Polyacrylonitrile (PAN, weight averaged molecular weight $M_w \sim 150,000$, Sigma–Aldrich, batch number MKBD3387), N,N-dimethylformamide (DMF, $\geq 99.8\%$, Sigma–Aldrich), and lithium chloride (LiCl, anhydrous, MP Biomed) were used as the polymer, the solvent, and the pore former, respectively, for casting membrane substrates. Sodium hydroxide (NaOH, $\geq 98\%$, anhydrous, pellets, Sigma–Aldrich) was used for PAN substrates treatment to improve their surface charge and hydrophilicity. Poly(allylamine hydrochloride) (PAH, average $M_w \sim 56,000$, Sigma–Aldrich) and poly(sodium 4-styrene-sulfonate) (PSS, average $M_w \sim 70,000$, 30 wt.% in H$_2$O, Sigma–Aldrich) were used during LbL assembly as the polycation and polyanion, respectively. The polyelectrolyte solution ionic strength was adjusted by sodium chloride (NaCl, 99%, Merck). Glutaraldehyde (GA, 25% in water, Sigma–Aldrich) was used as a crosslinker for the LbL membranes. Magnesium chloride (Merck) was used as draw solute during FO performance tests. Distilled water was used as the feed solution. All chemicals were used as received.

2.2. Fabrication of porous PAN substrates

The PAN substrate preparation method has been reported elsewhere [38]. Basically, PAN was dried in a vacuum oven at 50 °C for at least 12 h to remove moisture prior to the preparation of dope solutions. A pre-weighted amount of LiCl was dissolved into DMF in a jacket flask equipped with a mechanical stirrer, and then a desired amount of PAN was added into the flask followed by mixing for at

least 2 days at a temperature of 60 °C. The resulting polymer solution (PAN/LiCl/DMF at 18:2:80 weight ratio) was cooled down to room temperature, filtered, and degassed prior to film casting. PAN substrate was casted onto a glass plate with a stainless steel casting knife (Elcometer Pte Ltd., Asia). The gate height used in the current study (150 μm) was smaller than the one reported in our previous study (175 μm) [38], with the intention to further reduce the substrate thickness. The casted film was immediately immersed into tap water at room temperature for ~10 min till the PAN substrate was separated from the glass plate. The resulting membrane substrate (denoted as PAN-o) was washed in tap water bath followed by deionized (DI) water rinsing. To improve the substrate surface hydrophilicity and charge properties via partial hydrolysis, alkali solution post-treatment was conducted according to Ref. [38] by immersing the PAN-o substrate completely into a 1.5 M NaOH solution at 45 °C for 1.5 h, and the NaOH treated PAN membrane was designated as PAN-OH.

2.3. Layer by layer assembly and crosslinking

For LbL rejection layer preparation, the PAN-OH substrate was immersed into the polycation solution (1 g/L PAH/0.5 M NaCl solution) and polyanion solution (1 g/L PSS/0.5 M NaCl solution) in an alternative sequence [38]. The soaking time in each polyelectrolyte solution was 30 min and only the active face of the substrate was exposed to the solution. Each polyelectrolyte soaking step was also followed by a 1-min DI water rinsing step to remove excess polyelectrolyte molecules. In the current study, the PAH/PSS treatment was repeated to prepare membranes with one, two and three layers of PAH/PSS (denoted as LbL1, LbL2, and LbL3, respectively). Crosslinking of LbL FO membranes were performed by immersing LbL1, LbL2, and LbL3 in a 0.1 wt.% glutaraldehyde solution at room temperature for 2 h followed by 30-min washing with DI water [43]. The resultant crosslinked LbL membranes were designated as xLbL1, xLbL2, and xLbL3, respectively.

2.4. Membrane characterization and performance testing

Membrane cross section and surface morphologies were observed by Zeiss EVO 50 SEM according to Ref. [38]. Substrate porosity was measured based on gravimetric measurements of dry and wetted substrates according to Ref. [27]. A Perkin Elmer Spectrum 2000 ATR-FTIR spectroscope was used to confirm the chemical changes on the membrane surface before and after the crosslinking reaction. The detailed procedures on FTIR were reported elsewhere [44]. The membrane surface charge (zeta potential) was measured using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) in a 10 mM potassium chloride solution.

The membrane pure water permeability and salt rejection were determined in RO testing mode using a bench scale cross-flow RO filtration unit [22]. Compaction was performed at an applied pressure of 2.5 bar for 3 h prior to the measurement. The salt rejection was measured based on conductivity measurements (Mettler Toledo) using a feed water containing 500 ppm MgCl$_2$ at 2.5 bar with a cross flow velocity of ~20 cm/s.

The details of FO performance testing can be found elsewhere [38]. Briefly, FO tests were performed using a cross-flow FO test cell (effective membrane area of 42 cm^2) at 23 °C. The DS (MgCl$_2$ at various concentrations) and feed solution (DI water) were pumped with two independent variable-speed gear pumps, respectively. The volumetric flow rates for both FS and DS were 450 mL min^{-1} (cross flow velocity at 18.75 cm/s). The FO water flux was determined by measuring the weight change of the feed water using a digital mass balance connected to a data logging system. The solute flux was determined by monitoring the conductivity changes in the