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Influence of the properties of layer-by-layer active layers on forward osmosis performance

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ABSTRACT

The advancement of forward osmosis (FO) technology requires separation membranes with appropriate transport characteristics. The layer-by-layer (LbL) method exhibits great flexibility for fabricating the active layer of FO membrane with controllable separation properties. The current work focused on investigating the effect of LbL active layer properties on the FO performance. A series of FO membranes were prepared with varied number of polyelectrolyte bilayers which were composed of positively charged poly(allylamine hydrochloride) (PAH) and negatively charged poly(sodium 4-styrene-sulfonate) (PSS), with either PAH or PSS as the terminating layer. The active layers were characterized in terms of contact angle, surface roughness, and zeta potential, which were exploited to explain the variations of the intrinsic transport properties (the hydraulic permeability and the solute permeability) of the polyelectrolyte multilayer films. FO filtration experiments were carried out to assess the performance of the same series of FO membranes. Both the filtration flux and the FO efficiency were demonstrated as a strong function of the LbL active layers. This dependency was rationalized by analyzing the relative importance of the different transport mechanisms during the FO processes, which were inherently correlated to the intrinsic transport properties of the multilayer films. The current investigation not only justifies the feasibility of improving the FO performance by properly controlling the number of the polyelectrolyte bilayers and the surface charge, but also makes the underlying mechanisms comprehensible.

1. Introduction

Forward osmosis (FO) is an emergent membrane separation technology with potential applications in desalination [1–3], wastewater treatment [4], food processing [5], membrane bioreactor [6,7], and so on. One of the key factors limiting the development of FO technology is the fabrication of high performance FO membranes. Similar to conventional membranes for pressure-driven membrane processes (e.g., reverse osmosis and ultrafiltration), FO membranes are composed of a thin selective layer (active layer) and a porous support layer. However, the osmotically driven FO suffers from the loss of driving force caused by internal concentration polarization (ICP), i.e., the severe change of the solute concentration within the support layer. Previous studies [8–10] indicate that the extent of the ICP during FO processes strongly depends on the transport properties of FO membranes, which could be tuned by changing the microstructures of both the active layer and support layer.

As one of the electrostatic self-assembly (ESA) techniques [11,12], the layer-by-layer (LbL) method has been successfully applied to the fabrication of FO membranes [13–15]. In this method, the active layer is formed by depositing oppositely charged polyelectrolytes in an alternate sequence onto a porous substrate. The LbL method has the flexibility in controlling the permeation properties of the active layer with more degrees of freedom compared to the conventional phase inversion method [13]. In previous studies, attention was mainly given to the physicochemical properties of the LbL films, e.g., the surface water wettability [16], the zeta potential [17], and the solute diffusivity [18]. However, these studies are unable to provide direct information for optimizing the LbL active layer for enhancing the FO performance owing to the highly nonlinear transport phenomena in the support layer.

The objective of the current study was to correlate the properties of the LbL FO membranes to the filtration performance during FO processes. Lab-scale FO membrane specimens were prepared by LbL method. A series of characterization experiments were carried out to determine the properties of the active layers as a function

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of the number of the polyelectrolyte bilayers. Based on these characterization results, the effects of the LbL layer active layers on the FO performance will be analyzed in conjunction with the FO filtration experimental data, and implications on optimizing the LbL method for FO membrane will be discussed.

2. Experimental

2.1. Membrane fabrication

The polyacrylonitrile (PAN) substrate was fabricated using the phase inversion method as introduced in our previous work [13–15]. Specifically, the polymer solution was prepared by dissolving PAN (weight averaged molecular weight $M_w \sim 150{,}000$, Sigma-Aldrich) and Lithium chloride (LiCl, anhydrous, MP Biomed) into N,N-dimethylformamide (DMF, $\geq 99.8\%$, Sigma-Aldrich) with a mass ratio of 18:2:80. The degassed polymer solution was cast onto a flat glass plate by a stainless steel casting knife (Elcometer Pte Ltd, Asia) with a gate height of 150 μm. Then, the cast polymer film was immediately immersed into tap water at room temperature ~20 °C, and the porous polymer structure was formed via the phase separation. After the immersion precipitation, the PAN polymer film was washed by fresh tap water followed by a rinse of DI water. In order to impart the negative charge and enhance the hydrophilicity, the prepared PAN substrate was soaked in the alkali solution of 1.5 M NaOH (anhydrous, pellets $\geq 98\%$, Sigma-Aldrich) at 45 °C for 1.5 h. Specially, the PAN substrate with NaOH treatment was designated as PAN-OH substrate [13,14]. Besides, the hydrophilicity of the PAN-OH substrate [19] and its finger-like porous structure (see Fig. A1 in Appendix and [13–15]) also help to improve the mass transfer inside the substrate.

The polycation and polyanion solutions were prepared by dissolving poly(allylamine hydrochloride) (PAH, average $M_w \sim 112{,}000$ to 200,000, Polyscience) and poly(sodium 4-styrene-sulfonate) (PSS, average $M_w \sim 70{,}000$ 30 wt% in water, Sigma-Aldrich), respectively, into NaCl (99%, Merck) solution of 0.5 M. Then, the polyelectrolyte bilayers were formed by alternately exposing the surface of negatively charged PAN-OH substrate to the PAH and PSS solutions. The duration of each exposure in the polyelectrolyte solution was 30 min, and each adsorption was followed by a rinse of DI water for one minute. As indicated by our previous studies [13,14], the electrolyte rejection of the LbL skin layer might be substantially reduced in high ionic strength surroundings owing to the Donnan exclusion effect. To reduce such adverse effect, the chemical crosslinking of LbL active layer with glutaraldehyde (GA, 25% in water, Sigma-Aldrich) was performed following our previous study [14]. In particular, we denoted the crosslinked LbL membranes by xLbLn, in which n represents the number of the electrolyte bilayers. According to this notation, for example, xLbL3.0 has 3 PAH/PSS bilayers and the outmost layer (terminating layer) is PSS; xLbL3.5 has one more PAH coating (i.e., half of a bilayer) in addition to the 3 PAH/PSS bilayers, with PAH being the terminating layer. In the current study, we prepared three PSS-terminated (T-PSS) active layers (xLbL1.0, xLbL2.0, and xLbL3.0) and four PAH-terminated (T-PAH) active layers (xLbL0.5, xLbL1.5, xLbL2.5, and xLbL3.5).

2.2. Membrane characterization

Three different measurements were implemented for determining the surface characteristics of the prepared xLbL active layers. First, an OCA contact angle system (DataPhysics Instruments GmbH, Germany) was employed to measure the contact angle on the surface of the outmost polyelectrolyte films. Specifically, the sessile drop method [13,20] was adopted for the contact angle measurement, and the measurement was repeated 14 times for individual membrane specimens. The surface roughness was detected using an atomic force microscope (AFM, Park system, Korea) with the noncontact mode. The scan area was 25 μm^2, and the scan rate was varied from 0.5 to 1.0 Hz. The measured roughness for each membrane sample was the average value from 4 different samples. Finally, the zeta potential was measured with an eletrokinetic analyzer (EKA, SurPASS, Anton Paar GmbH, Austria) using a 10 mM NaCl background electrolyte. The zeta potential values were given by the best fittings with the Helmoltz–Smoluchowski equation [13], and the measurement for each membrane sample was repeated 4 times.

The intrinsic transport properties of the xLbL active layers were measured by performing the reverse osmosis (RO) filtrations. The bench-scale filtration setup was equipped with the membrane cell of effective area 42 cm^2. Prior to each measurement, the membrane specimens were compacted with an applied pressure of 5 bars for at least 3 h. In the measurements for the hydraulic permeability A, pure water was used as the feed to determine the bulk flux J_V as a function of the transmembrane hydraulic pressures ΔP. Then, the value of A was obtained by the linear fitting of J_V versus ΔP. As revealed in the literature [1,8], the effect of the ICP on RO processes could be neglected since RO processes are mainly driven by the hydraulic pressure difference. Therefore, the values of the solute permeability B for a variety electrolyte solutes were obtained by fitting the RO filtration experimental results with the formula $B = A(\Delta P - \Delta\pi)(1/R - 1)$ [13], where $\Delta\pi$ is the osmotic pressure difference across the membrane, and R is the apparent solute rejection based on conductivity measurement (Ultrameter II, Myron L Company, Carlsbad, CA). Four electrolyte solutions were employed as the feed solution: 5 mM $MgCl_2$, 7.5 mM $MgSO_4$, 5 mM Na_2SO_4, and 7.5 mM NaCl (all were purchased from Merck). All the filtrations were run with an applied pressure of 5 bars, and a cross flow rate of ~20 cm/s for the feed stream was adopted to minimize the external concentration polarization (ECP).

2.3. Evaluation of FO performance

The FO filtration was implemented by applying the draw solution (DS, the phase of high osmotic pressure) and the feed solution (FS, the phase of low osmotic pressure) to the different sides of the FO membrane, and the bulk flow (water) was thus driven from the FS side to the DS side. In the current filtration experiments, the feed solution was DI water while the draw solution was a series of solitary electrolyte solutions, including $MgCl_2$, $MgSO_4$, and Na_2SO_4. With the aid of the thermophysical modeling software (OLI Stream Analyzer 3.1, Morris Plains, NJ), the concentration of the each electrolyte was varied so that the osmotic pressure holds the value of 38 bars. The FO membranes were accommodated in an FO membrane cell with an effective area of 42 cm^2, and both DS and FS streams were pumped into the cell with a counter-current mode. The cross flow velocities for both streams were set at ~18.75 cm/s so as to minimize the effect of ECP [13]. The change of the FS weight was recorded as a function of filtration time, which was then used to determine the bulk flux. In particular, two membrane orientations were adopted, i.e., the orientation with the active layer exposed to the draw solution (AL-DS) and the orientation with the active layer facing the feed solution (AL-FS). All these FO filtration experiments were repeated 3 times for the same operating conditions.

3. Results and discussion

3.1. Surface characteristics of xLbL active layers

The surface characteristics of the xLbL active layers are of particular value to envisage the transport processes occurring at