Development of novel layer-by-layer assembled nanofiltration hollow fiber membranes for water treatment

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**DEVELOPMENT OF NOVEL LAYER-BY-LAYER
ASSEMBLED NANOFILTRATION HOLLOW
FIBER MEMBRANES FOR WATER
TREATMENT**

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School of Civil and Environmental Engineering

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PUBLICATIONS

Journal papers:

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Rajabzadeh Saeid, **Chang Liu**, Lei Shi, Rong Wang. "Preparation of low-pressure water softening hollow fiber membranes by polyelectrolyte deposition with two bilayers." Desalination, v 344, p 64-70, July 1, 2014.

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ABSTRACT

Membrane technology has been studied extensively for water treatment over decades. The layer-by-layer (LBL) assembly method, which involves the build-up of polyelectrolyte multilayer (PEM) films on the surface or inside the pore structure of various membrane substrates, has shown great potential due to its extremely low thickness, highly controllable performance and simple procedures of formation. Therefore, this study aims to develop high performance hollow fiber membranes using the LBL assembly method for forward osmosis (FO) and water softening processes. In FO process, low concentration draw solution (less than 0.5M) was used to substantially reduce the draw solution (DS) replenishment, and the energy consumption for draw solution regeneration and separation. While in the water softening process, low operating pressure (less than 5bar) would be more suitable for hollow fiber membrane configuration with reduced energy consumption.

With a solid understanding of the separation mechanisms of nanofiltration, a three-stage approach to develop the LBL assembled NF hollow fiber membrane has been adopted. At stage one, studies were conducted on the LBL deposition conditions to be applied on a polyethersulfone (PES) hollow fiber substrate. A simple deposition procedure by immersing the substrate into the polyanion poly(styrenesulfonic acid) (PSS) and polycation Poly(allylamine hydrochloride) (PAH) solutions alternately was used to achieve the desired number of deposition layers. With six layers of polyelectrolytes deposited, the membrane showed a high water flux of $40.5 \text{ l/m}^2 \text{ h}$ with a low salt to water flux ratio, J_s/J_v , of 0.201 g/L when using DI water as the feed and a 0.5 M MgCl_2 solution as the draw solutions in the active layer facing draw solution (AL-facing-DS) orientation. In addition, 14.6 and $25.9 \text{ l/m}^2 \text{ h}$ water fluxes with corresponding low J_s/J_v ratios of 0.034 and 0.066 g/L can be achieved using 0.05 and 0.1 M draw solution concentrations, respectively, suggesting great potential of the LBL hollow fibers in the FO process.

It is proved that the inner surface modification may possess several advantages over the shell side for the hollow fiber substrate such as better protection of selective layer, enhanced homogeneity and controllability of the chemical modification and

reduced chemical requirement. Therefore in the following study, inner skin deposited LBL (id-LBL) membranes were fabricated using a semi-dynamic process in which the solutions were introduced /replaced in the fiber lumen by syringes followed by static contact for a desired time. The newly developed id-LBL membranes were then tested in NF and FO applications and the performance were compared with outer surface deposition as well as some literature data. It was found that the id-LBL membranes could not only withstand higher operating pressure but also possess superior hardness rejection especially in high concentration mixed salt solutions (more than 95% rejection to Mg^{2+} and Ca^{2+} in a 5000 ppm total dissolved salt (TDS) mixture under 4.8 bar). As for the FO process, of only two layer deposition, the id-LBL membranes also demonstrated significant performance improvement with increased water flux (up to $70 \text{ l/m}^2 \text{ h}$ using 0.5 M MgCl_2 as draw solution in AL-facing-DS configuration) and reduced salt leakage (around $0.5 \text{ g/m}^2 \text{ h}$ using 1 M MgCl_2 draw solution in AL-facing-FW configuration). It suggested that for hollow fiber substrate, the inner surface was also more suitable for the formation of the selective layer via LBL deposition than the outer surface.

However, it was found later that the rejection of id-LBL membranes was drastically deteriorated in the presence of SO_4^{2-} in the feed water due to the weakened charge effect while the size exclusion was expected to play a more important role. Therefore, glutaraldehyde (GA) crosslinking was adopted in combination with modified LBL deposition conditions to develop a novel hollow fiber NF membrane with low-pressure water softening capability for synthesized hard water containing divalent counter ion SO_4^{2-} . Based on the membrane characterization results, the possible structure of the deposited layers and the effect of GA crosslink were proposed. It was found that the crosslinking could tighten the membrane surface pores with increased hydrophilicity while the membrane surface charge was reduced. The crosslinked LBL membrane showed more than $10 \text{ l/m}^2 \cdot \text{h} \cdot \text{bar}$ permeability with above 95% rejection to each of 1,000 ppm MgCl_2 , MgSO_4 and Na_2SO_4 solution under 2 bar pressure. It was also proven to be more suitable for the low-pressure water softening application at 2 bar in all tested feed water with the presence of SO_4^{2-} and TDS up to 10,000 ppm in terms of both permeability and

hardness removal efficiency when compared with commercial NF 270 and NF 90 membranes.

The future plans for this project are proposed in three directions: (1) to scale up the crosslinked LBL membrane with the best water softening performance for pilot study and possible commercialization; and (2) to explore the further applications of LBL hollow fiber membranes by modifying membrane properties such as surface pore size and charge density based on current PES substrate.; (3) to develop microfiltration (MF) hollow fiber substrate suitable for LBL deposition and explore the possible applications.

Keywords: composite membrane, layer-by-layer assembly, polyelectrolyte multilayers, crosslinking, forward osmosis, nanofiltration, water softening

CHAPTER 1 INTRODUCTION

1.1. Background

Due to its semi-permeable nature, membrane technology has been studied extensively for pressure-driven water treatment since the invention of Loeb-Sourirajan's asymmetric cellulose acetate (CA) membrane back to the late 1950s. The breakthrough point for the membrane technology implementation in the small-molecule separation occurred in the early 1970s, after the development of the composite membrane (Riley et al. 1971). In this type of membrane, different materials can be utilized to form two major structural components: the relatively thin selective layer with high selectivity and the porous support which provides mechanical strength with minimized permeation resistance. One of the typical composite membrane fabrication technologies is the interfacial polymerization to form an aromatic polyamide selective layer on a polymeric membrane support which dominates the current commercial membrane market (Lee et al. 2011).

Based on the membrane pore size and the types of retained substance, membranes can be classified into four major categories which are listed in Table 1-1. Among them, microfiltration (MF) and ultrafiltration (UF) membranes are considered as porous membranes with pore size larger than 10 nm (Mulder 1996). High permeation flux can be achieved under low operating pressure in these two processes and the retention of components is based on the sieving mechanism. In contrast, reverse osmosis (RO) membranes are non-porous and the permeation across the membrane is based on the solution-diffusion mechanism. Therefore, the RO membrane possesses the highest rejection towards the monovalent ions but also requires the highest operation pressure.

Table 1-1. Characteristics of membranes for pressure-driven processes (Schäfer et al. 2005).

Membrane	Separation mechanism	Pore size	Operating pressure	Removes
MF	Size exclusion	0.1-10 μm	<2 bar	Suspended solids/ bacteria
UF	Size exclusion	10-100 nm	1-5 bar	Macromolecules/ viruses
NF	Size exclusion/ electrical exclusion	0.5-2 nm	5-20 bar	Multivalent ions/ natural organic matters
RO	Solution-diffusion	<0.5 nm	10-100 bar	Monovalent ions/ small organics

Nanofiltration (NF) was first recognized in the late 1980s with the definition of “a process intermediate between reverse osmosis and ultrafiltration that rejects molecules which have a size in the order of one nanometer” (Eriksson 1988). The NF membrane possesses a pore size typically around 1 nm with a molecular weight cut-off (MWCO) of 300-500 Da. In addition, NF membranes are generally negatively or positively charged so that the separation mechanisms of NF membranes involve both steric (size exclusion) and electrostatic (Donnan exclusion) effects. Most of the commercial NF membranes are thin film composite (TFC) flat sheet membranes made from interfacial polymerization such as NF series by Dow, UTC series from Toray and Desal series by GE-Osmonics. Meanwhile, a variety of methods were also proposed by researchers to fabricate NF membranes for applications in many areas such as water and wastewater treatment, pharmaceutical and food industries.

Over the past two decades, the layer-by-layer (LBL) assembly method, which involves the buildup of polyelectrolyte multilayer (PEM) films on the surface or inside the pore structure of various membrane substrates, has shown great potential to form NF membranes for its extremely low thickness, highly controllable performance and simple formation procedures (Meier-Haack et al. 2001; Xiao et al. 2001; Jin et al. 2003; Malaisamy and Bruening 2005). In a typical LBL process, the supporting substrate is immersed into the aqueous solutions of positively and

negatively charged polyelectrolytes alternately. Based on the electrostatic attraction between the polycation and polyanion pairs, the multilayer film is formed on the substrate with precise control over its thickness and structure and therefore the membrane performance.

1.2. Limitations for NF and LBL assembled membranes

Although NF membranes have shown promising perspectives in water treatment with a wide range of applications, there are still some prevalent issues that hinder the further development of this technology. Six major challenges for current NF membranes have been identified in one of the state-of-art review papers (Van der Bruggen et al. 2008), including: (1) membrane fouling and possible remedies, (2) improved separation between solutes, (3) further treatment of concentrates, (4) chemical resistance and limited lifetime of membranes, (5) insufficient rejection of undesired substance, and (6) the need for simulation and modeling tools. Among them, the high rejection of divalent ions such as Mg^{2+} and Ca^{2+} is the critical requirement for a good NF membrane in many applications such as forward osmosis (FO) and water softening process. In addition, the high separation between divalent ions and Na^+ is also crucial to achieve the low pressure operation of water softening process where the divalent ions are rejected by the membrane for the softening purpose while the passage of Na^+ through the membrane can significantly reduce the osmotic burdens. Therefore, they will be the key design parameters in the development of LBL NF membranes in this study.

Up to now, a number of LBL deposition based products have been found on the market such as coatings for contact lenses (Ciba Vision) and coatings for chromatography columns (Agilent). However, there is still no successful commercial application of LBL assembled membranes despite that they have shown a wide range of attractive properties. Although the LBL deposition seems to be easy in the lab experiments, it is still unclear whether the same procedures would be suitable and economical to be applied at large scale. Moreover, due to the nano-scale nature of the PEM films, there is a lack of adequate fundamental studies and

direct observation methods for a more comprehensive understanding of the process. Last but not least, the development of appropriate supports especially polymeric hollow fibers is another challenge in the further improvement of membrane performance.

1.3. Objectives

This study aims to develop high performance NF hollow fiber membranes using LBL assembly method for different water treatment applications such as FO using low concentration draw solutions and low pressure water softening. The primary objectives for this study include:

- 1) to prepare composite NF membrane by LBL assembly on the polyethersulfone (PES) UF hollow fiber substrate;
- 2) to study the deposition conditions and LBL membrane characteristics in order to provide theoretical guidance for membrane performance optimization;
- 3) to fabricate LBL membrane to achieve high water flux and low reverse salt flux using low concentration draw solutions in FO processes;
- 4) to fabricate LBL membrane to maintain high hardness removal with high permeation flux against high (Mg^{2+} , Ca^{2+} , SO_4^{2-}) concentration feed water in low-pressure water softening processes.

1.4. Scope of the thesis

This thesis contains six chapters including an introduction, a literature review on polyelectrolyte multilayer (PEM) films, nanofiltration and forward osmosis processes, three-stage detailed experimental studies and discussions, conclusions and recommendations for future work.

In Chapter 2, the literature review covers three different aspects. The PEM films, as the fundamental building blocks for the LBL assembled membranes, are introduced first, which include the choices of polyelectrolytes and substrate, formation mechanism, structure properties and performance-affecting parameters. In the next part, an overview of applications of PEM films including the LBL assembled membranes is provided. In part three, two major applications in this study, namely the nanofiltration (water softening) and forward osmosis, are briefly discussed.

In Chapter 3, the fabrication of the outer surface deposited LBL hollow fiber membranes was developed, and their performances in forward osmosis process using low concentration draw solutions in both configurations, the active layer facing draw solution (AL-facing-DS) and the active layer facing feed water (AL-facing-FW), were evaluated and the discussed in detail.

In Chapter 4, the LBL deposition was performed at the inner surface of the PES hollow fibre substrate to form a composite NF membrane. The semi-dynamic deposition procedure was adopted. The newly developed inner deposited (id-LBL) membranes were then tested in NF and FO applications and the performance were compared with outer surface deposited membranes as well as some literature data.

In Chapter 5, the glutaraldehyde (GA) crosslinking was applied on the LBL NF hollow fiber membrane to enhance its water softening performance in the presence of divalent counter ion SO_4^{2-} . The characteristics of the crosslinked membranes were studied thoroughly and their water softening performance were compared with uncrosslinked ones as well as two commercial flat sheet NF membranes NF 90 and NF 270.

In Chapter 6, a general summary of the thesis is provided with the proposed future plans for this project in three directions: (1) to scale up the crosslinked LBL membrane with the best water softening performance for pilot study and possible commercialization; and (2) to explore the further applications of LBL hollow fiber membranes by modifying membrane properties such as surface pore size and charge densities based on current PES substrate; (3) to develop microfiltration (MF) hollow

fiber substrate suitable for LBL deposition and explore the possible applications. All approaches will be briefly introduced here with some preliminary results.

CHAPTER 2 LITERATURE REVIEW

2.1. Polyelectrolyte multilayer (PEM) films

The use of alternating adsorption of anionic and cationic polyelectrolytes to form a multilayer film was first proposed by Decher, etc. in the early 1990's (Decher et al. 1992). In the article, the authors demonstrated the build-up of the PEM films on a positively charged quartz or silicon substrate in a "layer-by-layer" (LBL) manner and proved the linear growth of film thickness with the number of deposition steps by X-ray reflectivity monitoring. For its versatility and simplicity, the LBL deposition technique was rapidly extended to other multi-topic molecules presenting mutually interacting binding sites (Michel et al. 2012) such as polymers carrying hydrogen donor and acceptor moieties (Kharlampieva et al.), stereoregular polymers carrying sites of opposite chirality (Kamei et al.) and π - π interactions between molecules carrying aromatic cycles and carbon nanotubes (Zhu et al. 2011). In this work, the LBL deposition is restricted to the formation of the PEM films based on the oppositely charged polyelectrolytes only. A general review will be provided with information on the choice of polyelectrolytes and substrates, formation and structure of the PEM films, the performance affecting parameters and the application of PEM films.

2.1.1. Polyelectrolyte and substrate for LBL assembly

The word 'polyelectrolyte' is the combination of 'polymer' and 'electrolyte', which describes a special group of polymers containing at least one electrolyte group in each repeating unit that can be dissociated and charged in water or other aqueous solutions. Some commercially available polyelectrolytes commonly used in the literature are listed in Figure 2-1 including (1) poly(acrylic acid) (PAA), (2) poly(vinyl sulfate) (PVS), (3) poly(styrene sulfonate) (PSS), (4) poly(ethylenimine) (PEI), (5) poly(allylamine) (PAAm), and (6) poly(diallyldimethylammonium chloride) (PDADMAC).

Figure 2-1. Some commonly used polyelectrolytes for LBL assembly.

The most critical criterion for the selection of appropriate polyelectrolyte is the charge density ρ_c defined by the number ratio of ion pairs and carbon atoms per repeat unit of the polyelectrolyte (Tieke et al. 2001). However the definition of ρ_c neglects any contribution from specific structural elements such as the flexibility of the main chain and the side groups, the presence of aromatic or aliphatic units, and different polar groups in the polyelectrolytes. The performance correlation was still solid as in general the flux was inversely proportional to ρ_c and a high separation was obtained if the charge density of the PEM network was high.

Theoretically, any polyelectrolyte pairs containing critical minimum charge density to support successful multilayer growth can be used in LBL assembly (Bertrand et al. 2000). However, other properties of the selected polyelectrolyte have to be taken into consideration in real applications. One of the most important criteria is the appropriate matching of charge density for the polyelectrolyte pairs (Fischer et al. 1999). In other words, one highly charged polyelectrolyte has to be matched with a partner carrying at least intermediate density of opposite charges for favorable film growth. The unmatched pairs may result in non-uniform and non-reproducible build-up of layers or even preclude from film formation.

Another important consideration is the choice of strong and weak polyelectrolytes. Here, the ‘strong’ and ‘weak’ refer to whether the charge groups on the polymer are

permanent or in responsible to the pH of the solution. Choi and Rubner summarized and plotted the degree of ionization of negatively charged PAA and positively charged PAH as a function of solution pH (Choi and Rubner 2005), as shown in Figure 2-2. Drastic variations of the charge density were observed for both weak polyelectrolytes. Therefore the pH of the solution is one of the key parameters to determine the performance of the PEM multilayers containing weak polyelectrolytes, which will be discussed in detail at the later part of this literature review. The other properties of the polyelectrolyte such as the molecular weight, hydrophobicity and additional functionally groups may also affect the LBL assembly to a certain extent (Schonhoff 2003).

Figure 2-2. Degree of ionization of PAA and PAH in solution as a function of pH (Choi and Rubner 2005).

It is believed that the LBL deposition can be simply carried out on essentially any substrate that supports the adsorption of the initial layer of polymer (Bruening et al. 2008). The influence of the substrate surface chemistry is pronounced on the first few deposited layers while the further deposition is not influenced by the substrate once the surface coverage reaches a critical level (Michel et al. 2012). Therefore, in the phenomenological and theoretical studies, the choice of the planar substrate is mainly based on the convenience for particular analytical method (Bertrand et al. 2000). Glass, quartz, silicon wafers, and alumina are among the most popular materials used. For instance, the silicon wafers have been widely used for the ellipsometric thickness determination (Schlenoff and Dubas 2001; Stanton et al. 2003; Itano et al. 2005) and X-ray reflectivity (Steitz et al. 2001) for their smooth surface. While glass and gold coated quartz can be used for small angle X-ray

(Lowack and Helm 1998) and quartz crystal microbalance with dissipation (QCM-D) measurement (Elzieciak et al. 2009) respectively.

On the other hand, the polymeric substrates are more suitable for practical applications because of their variety and porous structure. In most studies the substrates are either positively or negatively charged, inherently or created by surface treatment, due to the charged nature of the LBL assembly. Some common surface modifications including oxidation (Schlenoff et al. 1998) and plasma treatment (Krasemann and Tieke 1998) are applied on the hydrophobic polymers before the initial polyelectrolyte deposition to create desired number of charged groups. However, it has been proven at later stage where the successful adsorption of multilayers can also be achieved by polar or hydrophobic interaction on some uncharged polymeric substrates containing carbonyl groups or benzene rings (Delcorte et al. 1997). For example, Malaisamy and Bruening were able to perform LBL assembly on the polyethersulfone (PES) ultrafiltration membrane substrate based on the hydrophobic interaction with the PSS as the starting layer (Malaisamy and Bruening 2005). Moreover, the LBL deposition can be also applied to colloids and nanoparticles. Some of these examples can be found in the section 2.2 on the application of PEM films.

2.1.2. Formation and structure of PEM films

For the first layer deposition, the amount of polyelectrolyte adsorbed on the substrate surface is mainly depends on (1) the charge density of both surface and polymer chains for charged surface (Schonhoff 2003); and (2) available polar or hydrophobic pairing sites for uncharged surface (Bertrand et al. 2000). The adsorption of the rest of the layers differs significantly from the first layer because of the flexible chains on the underlying layers and the third direction (normal to the surface) charge distribution on them. Generally speaking, it can be considered as an ion exchange phenomenon where small ions (normally the salt ions) on the as-formed layer are replaced by charged segments of incoming polyelectrolyte polymers (Dubas and Schlenoff 1999) as in Eq. (2.1)

Where Pol^- and Pol^+ are charged polymer segments, A^+ and B^- are salt counter-ions and the subscript “m” and “aq” refers to the membrane surface and aqueous solutions respectively.

After each deposition, the charges on the outmost layer are normally compensated in three ways and their fraction depends strongly on the molecular structure of the polyelectrolyte pairs (Schonhoff 2003). The electrophoretic finger-printing (Donath et al. 1997) as well as the spin relaxation and zeta-potential studies (Schwarz and Schonhoff 2002) confirmed this theory and suggested the charges were almost equally compensated in each fraction in some of the PAH/PSS systems. Among them, the first portion complex with the internal charges on the underlying layer leading to the entanglement and interpenetration of the polymer segments; and the second portion neutralizes the surface charges of the previous layer both by the ion exchange process mentioned earlier. These two interactions form the $Pol^- Pol_m^+$ in Eq (2.1) which are irreversible under normal conditions. The last portion of segments form loops and tails extending to the solution resulting in the reversal of surface potential as the so-called charge overcompensation phenomenon. The free charges are compensated by the counter-ions in the solution to form $Pol^+ B_m^-$ and the B_m^- are then replaced again by Pol^- upon adsorption of the next layer. The charge overcompensation is expected in most cases if the segments interpenetration is not too high but the reversal of the surface potential is not necessary for the multilayer built-up in some references (Cini et al. 2010; Qi et al. 2012) as well as in the current studies.

Although the time scales for the multilayer formation may vary largely, it is generally accepted a two-step process is involved in most cases (Plech et al. 2000; Schonhoff 2003). In the first kinetic step, polyelectrolyte polymers move towards the substrate surface from the bulk solution followed by a fast mass deposition within seconds to minutes. This process ends up with the build-up of sufficient repulsive ζ -potential on the surface to prevent further adsorption and the rate of deposition is mainly determined by the diffusivity of polyelectrolytes (Plech et al.

2000). The second step usually lasts over hours where slow chain rearrangements take place through the entire structure. During this process, the polymer segments diffuse into the inner regions of the previously deposited layer to form an irreversible complexation of positive and negative segments (Dubas and Schlenoff 1999). Therefore, the as-formed PEM is an amorphous stratified layer without a distinctive layered structure which is confirmed by both x-ray reflectivity (Decher et al. 1994) and neutron reflectivity (Schmitt et al. 1993) experiments. A schematic drawing of the multilayer structure is presented in Figure 2-3.

Figure 2-3. Schematic drawing of PEM for (A) idealized layered structure and (B) amorphous stratified layers in reality

In most cases the film growth rate is a linear function on the numbers of deposited polyelectrolyte pairs and the film thickness increases in the order of a few nanometers which roughly equals to the sum of the characteristic size of polycation and the polyanion (Michel et al. 2012). The single layer thickness can be adjusted precisely by modifying the conformation of polyelectrolytes in their respective deposition solutions. The most common practice is to modify the polymer intramolecular structure by altering solution ionic strength or change the charge density of the weak polyelectrolyte by the pH of the solution. Both methods will be discussed in detail in next section.

2.1.3. Parameters affecting PEM films performance

Besides the appropriate choices of polyelectrolyte and substrate, there are a number of other parameters that affect the final performance of the PEM films. The solution ionic strength and pH of the weak polyelectrolyte solution have the most prominent effect which will be discussed in this section. Some other parameters such as the

concentration of the polyelectrolyte, drying procedure and solvent quality are either not applicable or have a marginal effect in water-based applications and thus will not be covered herein.

The ionic strength of the solution is normally adjusted by adding electrolytes such as NaCl into the polyelectrolyte solution before LBL assembly. The presence of the salt alters the conformation of the polymer chains in such a way that, without salt, the polymer chains are oriented flat and parallel to the substrate due to the electrostatic repulsion of the like charges; with the increasing salt concentration, the chains start to form coils with larger thickness as the increased screening of charges along the polymers (Bohmer et al. 1990). Therefore the total thickness of the deposited films can be adjusted precisely by adjusting the ionic strength of each polyelectrolyte solution. Various power laws of the layer thickness in dependence of the salt concentration were proposed for different systems such as a linear dependence on C_{salt} (Dubas and Schlenoff 1999), a scale with C_{salt}^{α} with $\alpha=0.5$ (Ruths et al. 2000) or an exponential scale of 0.05-0.15 (Ladam et al. 1999). In addition, the surface roughness of the PEM films is also typically increased with salt concentration according to the atomic force microscopy studies (McAloney et al. 2001).

As mentioned earlier, the pH value of the weak polyelectrolyte solution affect the formation of PEM film greatly by the variation of the charge density (fraction of charged segments) along the polymer chains which has a similar effect as the adding of salts (Kolarik et al. 1999). With less charged groups so with the self-repulsion forces, the polymer chains remain uncoiled to form thin layers and vice versa. Therefore, for a weak/strong polyelectrolyte pair (like PAH/PSS), the pH of weak polyelectrolyte solution is the major concern but the complexation arises when two weak polyelectrolytes (like PAA/PAH) are involved. For instance, the amine group of PAH becomes fully protonated below pH 4 with only around 30% charge remains at pH 10; oppositely, the ionization of carboxyl group on the PAA reaches almost 100% at pH 10 with only 10% at pH 4. Therefore, drastic changes in the total thickness of PEM films can be induced by a very small change in the pH of each solution (Shiratori and Rubner 2000) as shown in Figure 2-4. In this case, an

optimum pH for film preparation is proposed to be based on the mean pK_a value of the cationic and anionic groups of the polyelectrolytes.

Figure 2-4. Bilayer thickness of PAA/PAH in as a function of solution pH.
(Shiratori and Rubner 2000)

2.2. Application of PEM films

The PEM films have been receiving enormous attention for their simplicity and versatility in many areas such as drug delivery (Jewell and Lynn 2008; Silva et al. 2008), biology (Meyer et al. 2008; An et al. 2009), and optical devices (Wu et al. 1999; Dubas et al. 2006), etc.. In this section, three major applications: the responsive PEM films, LBL templating technique and LBL assembled membranes will be introduced briefly.

2.2.1. Responsive PEM films

One of the unique features of the PEM films is their responsive ability to various post-deposition environmental stimulus. The pH and ionic strength have been widely explored to trigger morphological changes in films deposited on flat substrates or to control permeability of PEM capsules to both low molecular compounds and macromolecules (Sukhishvili 2005). For example, the pH effect on the formation of large pores was demonstrated for both PEM capsules and films (Mendelsohn et al. 2000) while the effect of both pH and ionic strength on the permeability of PEM capsules to a low molecular dye was established experimentally (Antipov et al. 2003). In addition, Sui and Schlenoff were able to separate both acidic and basic proteins through the control of electroosmotic flow in microchannels by utilizing the pH-induced excessive charges on the film (Sui and Schlenoff 2003).

The incorporation of the bioactive molecules on the PEM films also draws increasing attention in different areas. The collagen contained PEM films have been used to coat cytotoxic materials to provide biocompatibility (Sinani et al. 2003) and the binding of certain enzymes are promising in the detection of a wide range of highly toxic compounds as enzymatic sensors (Constantine et al. 2003). In the controlled release application, the self-assembled polycation was used to trigger DNA releasing from PEM films in its native form by hydrolytic degradation (Vazquez et al. 2002). Meanwhile, the temperature (Serpe et al. 2003), magnetic responsive (Lu et al. 2005) and photosensitive (Skirtach et al. 2004) multilayers have also been investigated for different applications.

2.2.2. Template synthesis of nanostructured materials

The LBL templating techniques, first proposed by Caruso in 2000 (Caruso 2000), is the combination of template and LBL assembly technique to fabricate free-standing nanostructured materials with different morphologies and functions. In this process, various materials such as polymers, nanoparticles and proteins are binding on/in the

PEM films. The templating substrates, either planar or colloidal, are then removed to give rise to various nanostructured materials as illustrated in the schematic drawing (Figure. 2-5) by the same research group (Wang et al. 2007).

Figure 2-5. Schematic illustration of various nanostructured materials prepared by LBL templating technique (Wang et al. 2007).

The free standing films and nanotubes can be prepared by using planar templates as shown at the upper part of Figure 2-5. For instance, Jiang and co-workers (Jiang et al. 2004) successfully fabricated free standing PEM films with gold nanoparticles by dissolving the cellulose acetate substrate with acetone; and the anodic aluminium oxide membranes with cylindrical nanopores have been used by some groups to prepare various nanotubes from different materials like the protein/polyelectrolyte (Cui et al. 2006) and titania-based composites (Guo et al. 2005). Likewise, capsules, nanotubes, macroporous and nanoporous particles (as shown in anti-clockwise direction in the lower part of figure. 2-5) can also be produced by using colloidal templates for different applications.

2.2.3. LBL assembled membranes

The LBL assembly technique has been applied on or in the porous membrane substrates since the late 1990's. Compared with the traditional Langmuir-Blodgett thin-film deposition method, the ease of film formation, the film stability and versatility are the main strengths of this new technique (Bruening et al. 2008).

The most traditional LBL deposition procedure is the alternately dip coating method which involves the immersion of a substrate into polyelectrolyte solutions with opposite charges alternately with rising steps in between. This is a straightforward method which was also automated at the later stage (Krogman et al. 2007). However, it is time consuming since each deposition step needs at least a few minutes to complete. To speed up the process, alternated spray deposition (Schlenoff et al. 2000) and spin-coating methods (Chiarelli et al. 2002) were invented which require only seconds of deposition time. Yet, most of those studies were focused on the inorganic substrate or flat sheet membranes only. As for the hollow fiber membrane substrate, only a few research groups investigated the possibility of applying LBL deposition on the inner surface of a hollow fiber substrate. The common practice involves running the polyelectrolyte solution through the substrate lumen with (Kochan et al. 2009; Ouyang et al. 2010) or without (Su et al. 2012) applied pressure or even with negative pressure (Zhang et al. 2008; Wang et al. 2013) at the shell side.

Based on the combination of various polyelectrolyte pairs and substrates, the LBL assembled membranes are studied in a wide range of applications as shown in Table 2-1. Among all, the separation membrane and membrane absorber are two typical LBL membranes achieved by surface and pore modification respectively which will be briefly discussed below.

Table 2-1. Some applications of LBL assembled membranes.

Membranes	Supports	Applications	Ref.
(PSS/PAH) ₅	Porous alumina	nanofiltration	(Stanton et al. 2003)
(PEI/PAA) ₄	PES	pervaporation	(Kusumocahyo et al. 2002)
(PAH/PSS) ₅	Porous alumina	Cl ⁻ /Fe(CN) ₆ ³⁻ separation	(Krasemann and Tieke. 2000)
(PAH/PSS) ₇	Porous alumina	neutral molecule separation	(Liu and Bruening. 2004)
(PAH/PSS) ₅	Nafion	fuel cell	(Daiko et al. 2008)
(PAH/PSS) ₆	PAN-OH	forward osmosis	(Saren et al. 2011)
Poly(L-lysine) /PSS/PAH	Nylon	protein immobilization	(Smuleac et al. 2006)

The LBL deposition is regarded to be one of the ideal candidates in the fabrication of composite separation membrane for its accurate control over the film thickness on a nanometer scale (Joseph et al. 2014). Due to their charged nature, the LBL membranes are capable of selective removal of multivalent ions from monovalent ions by the Donnan exclusion effect. In a series of studies conducted by Bruening's group (Stanton et al. 2003; Malaisamy and Bruening 2005; Hong et al. 2006; Ouyang et al. 2008), PEM films were successfully deposited on both porous alumina and commercial flat sheet PES membranes. Upon careful control of deposition conditions, relatively high selectivity of Cl⁻/SO₄²⁻ or Na⁺/Mg²⁺ with considerable water flux were achieved under nanofiltration (NF) operation. Besides, the LBL membranes can also be used to separate some other species in water treatment based on either electrostatic repulsion or size exclusion. Aravind et al. (Aravind et al. 2010) used chitosan/PSS multilayered membranes to treat paper mills and textile effluents with a considerable reduction in color and chemical oxygen demand. And in a recent study, the phosphate recovery was reported in the form of H₂PO₄⁻ with a Cl⁻/H₂PO₄⁻ selectivity of 310 and a flux of 13.53 m³/m²-day

at very low pressure (0.28 bar) by the deposition of PEI/PSS films on a nylon substrate (Disha et al. 2012).

In contrast, the membrane absorbers utilize much higher surface area inside the macroporous membranes to create more effective binding sites for the immobilization of other building blocks such as proteins or nanoparticles. Instead of the static immersion, the PEM buildup is accomplished by alternate permeation of polyelectrolyte solutions through the substrate under pressure (Hollman and Bhattacharyya 2004). One of the fundamental applications for such a membrane is to capture specific substances on PEM films such as protein purification (Xu and Bao 2003). Moreover, the functional groups of the newly incorporated building blocks can further expand the versatility of PEM membranes in other applications such as catalysis. For example, Datta et al. (Datta et al. 2008) successfully immobilized the enzyme glucose oxidase on the LBL assembled nylon-based membrane which showed much improved performance in the oxidation of glucose than the free enzymes.

2.3. Nanofiltration

NF is an extremely complex process and is dependent on the microhydrodynamic and interfacial events occurring at the membrane surface and within the membrane nanopores (Mohammad et al. 2015). Unlike the non-porous RO membranes, where mass transport is governed by solution-diffusion mechanism, rejection from NF membranes is attributed to a combination of steric, charge, dielectric and transport (diffusion and convection) effect. Various predictive models for the transportation through NF membranes have been developed based on the extended Nernst-Planck equation which describes the contributions from diffusion, electromigration and convection as the three terms in the right hand side of Equation 2.1

$$j_i = -D_{i,\infty} K_{i,d} \frac{dc_i}{dx} - \frac{z_i c_i D_{i,\infty} K_{i,d}}{RT} F \frac{d\psi_m}{dx} + K_{i,c} c_i V \quad (2.1)$$

where j is the solute flux, c is the solute concentration, D is the diffusivity, z is the valence of ion, ψ_m is the electric potential, $K_{i,c}$ and $K_{i,d}$ are hindrance factors for the convection and diffusion.

For uncharged solutes, only diffusive and convective flows affect the transportation which is purely based on the size exclusion. While for the charged species, apart from the size effect, the Donnan effect determines the attractive or repulsive interaction between those species and charged membrane surface as well as the charge equilibrium in the system (Donnan 1995). However, due to the near atomic length scales of the NF membrane selective layer coupled with limitations of current measurement technologies, there is a lack of detailed knowledge of the physical structure and electrical properties of the membrane which has resulted in uncertainty and significant debate over the true nature of the separation mechanisms (Schäfer et al. 2005).

Nevertheless, the distinguishing characteristics of NF membranes such as the ability to retain small organic molecules, high selectivity between multivalent and monovalent ions, higher flux and lower operating pressure compared to RO membranes promoted their applications in many areas especially for water and wastewater treatment (Sen et al. 2010; Musbah et al. 2013; Phuntsho et al. 2013), food and textile engineering (Luo et al. 2010; Liu et al. 2011; Andrade et al. 2014), pharmaceutical and biotechnology (Nghiem et al. 2005; Nghiem et al. 2005; Stanford and Weinberg 2010). Among them, the application of NF membranes in water softening processes will be highlighted in the next section as one of the main objectives in this study.

2.3.1 Water softening

Water hardness refers to the presence of calcium, magnesium and certain other metal cations in water system, which causes a variety of problems in either household water supply or industrial water systems, such as the buildup of lime-scale that fouls plumbing and promotes galvanic corrosion, and the formation of

membrane scaling in seawater desalination (Gabrielli et al. 2006). Water softening is a process to remove the water hardness from various water streams and the conventional methods include the lime-soda ash treatment and ion exchange resin (Ghizellaoui et al. 2005; Nanda et al. 2008). However, both methods have limitations where the former produces a large amount of waste sludge that requires a significant land use, while the latter increases sodium chloride content in the treated water and needs high concentration salt brine for resin regeneration. In contrast, nanofiltration (NF) membrane offers a promising alternative with higher efficiency and lower operating cost in the softening process of groundwater (Schaep et al. 1998; Gorenflo et al. 2003), brackish water (Abuhabib et al. 2012) and drinking water (Ghizellaoui et al. 2005) as well as in the pretreatment for seawater desalination (Linnikov and Podberezhnyi 1996; Hassan et al. 1998; Song et al. 2011).

It is well recognized that the separation of the ionic species using NF membrane is based on both size exclusion and electrostatic interaction. Intuitively, a NF membrane with a highly positive charged surface and relatively loose structure would be ideal for the water softening application, which can provide good water permeability and high rejection to multivalent cations. However, it is far more complicated in real applications due to the limited choice of suitable membranes and complex feed water conditions.

To date, most of the commercial flat sheet NF membranes are interfacially polymerized thin film composite polyamide membranes as summarized in Table 2-2 from a review paper (Mohammad et al. 2015). Due to the use of traditional materials for the fabrication, they are either neutral or negatively charged during normal aqueous processes (Cheng et al. 2011). Therefore tighter membranes with a relatively small pore structure were often used to maintain high retention towards the hardness ions mainly based on the size exclusion (Schaep et al. 1998; Reddy et al. 2005; Galanakis et al. 2012; Fatima et al. 2013). Consequently, the water flux was greatly sacrificed due to the undesired high salinity retention, which generates high osmotic pressure against the hydraulic pressure, and high mass transfer resistance for water. As a result, an elevated operating pressure was required for the process. For example, Elazhar et al. (Fatima et al. 2013) studied the softening

process of synthetic Moroccan ground water using NF90 membrane to achieve an average of 96% hardness removal, accompanied by a more than 80% Na^+ rejection. Thus the water permeability was only around $5 \text{ l/m}^2 \text{ h bar}$ at a minimal operating pressure of 10 bar. Meanwhile, NF270 membrane failed in the same process with only about 60% hardness removal. In the other water softening study on the Greece brackish groundwater using a commercial polypiperazine NF membrane (Galanakis et al. 2012), only moderate hardness retention (70-76%) was achieved with a permeate flux of $15\text{-}47 \text{ l/m}^2 \text{ h}$ under transmembrane pressure of 6-10 bar. The salinity retention in this case was still as high as 44 to 66%.

Table 2-2. Commercial NF membranes with specification of the manufactures

Membrane	Manufacturer	MWCO (Da)	Maximum temperature (°C)	pH range	Stabilized salt rejection (%)	Composition on top layer
NE270	Dow Filmtec ^a	200–400	45	2–11	>97%	Polyamide thin-film composite
NE200	Dow Filmtec ^a	200–400	45	3–10	50–65% CaCl ₂ 3% MgSO ₄ 5% Atrazine	Polyamide thin-film composite
NE90	Dow Filmtec ^a	200–400	45	3–10	85–95% NaCl	Polyamide thin-film composite
TS80	Trisep ^b	150	45	2–11	99%	Polyamide
TS40	Trisep ^b	200	50	3–10	99%	Poly(piperazineamide)
XA45	Trisep ^b	500	45	2–11	95%	Polyamide
UTC20	Toray ^c	180	35	3–10	60%	Poly(piperazineamide)
TK60	Toray ^c	400	35	3–8	55%	Cross-linked polyamide composite
OK	GE Osmonics ^d	2000	30	3–6.5	94% MgSO ₄	Celulose acetate
DK	GE Osmonics ^d	200	50	3–9	98% MgSO ₄	Polyamide
DL	GE Osmonics ^d	150–300	90	1–11	96% MgSO ₄	Cross-linked aromatic polyamide
HL	GE Osmonics ^d	150–300	50	3–9	98% MgSO ₄	Cross-linked aromatic polyamide
NFX	Synder ^e	150–300	50	3–10.5	99% MgSO ₄	Proprietary polyamide thin-film composite
NFW	Synder ^e	300–500	50	3–10.5	40% NaCl	Proprietary polyamide thin-film composite
NFC	Synder ^e	600–800	50	4–10	97% MgSO ₄ /40% 20% NaCl	Proprietary polyamide thin-film composite
TFC SR100	Koch ^f	200	50	4–10	50% MgSO ₄ 10% NaCl	Proprietary thin-film composite polyamide
SR30	Koch ^f	200	50	4–10	>99%	Proprietary thin-film composite polyamide
SPRABRO	Koch ^f	200	50	3–10	99%	Proprietary thin-film composite polyamide
ESNA1	Nitto-Denki ^g	100–300	45	2–10	89%	Composite polyamide
NTR450	Nitto-Denki ^g	600–800	40	2–14	50%	Sulfonated polyethersulfone

^a Midland, Michigan, USA
^b Cadiz, CA, USA
^c Tokyo, Japan
^d Le Mee sur Seine
^e Vacaville, CA, USA
^f Wilmington, Massachusetts, USA
^g Saitama, Japan
^h Saitama, Japan

Over the past decades, various membrane fabrication methods have been proposed to produce positively charged NF membranes with water softening capability, including graft polymerization, interfacial polymerization using alternative monomers and surface modification with different positively charged chemicals. Ji et al. (Ji et al. 2012) introduced zwitterionic tri-polymers P(DMC-HEA-DMAPS) (PDHD) composed of 2-methacryloyloxy ethyl trimethylammonium chloride (DMC), 2-hydroxyethyl acrylate (HEA) and 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS) into NF membranes via the combination of surface coating and chemical crosslinking with glutaraldehyde (GA). By optimizing the reaction conditions, they could achieve a 96.5% MgCl_2 (1000 ppm) rejection and a flux of $47.8 \text{ l/m}^2 \text{ h}$ at 6 bar; Deng and co-workers (Deng et al. 2011) produced a NF membrane by UV-initiated graft polymerization of DMC onto polysulfone membranes. The resultant membranes demonstrated a 94.8% MgCl_2 (1000 ppm) rejection accompanied with a flux of $20.3 \text{ l/m}^2 \text{ h}$ at 2 bar; Very recently, dual layer composite nanofiltration hollow fiber membranes (Setiawan et al. 2014) and interfacially polymerized composite NF hollow fiber membranes (Fang et al. 2013) for low-pressure water softening were also reported.

As mentioned earlier on, the LBL membranes are capable of selective removal of multivalent ions from monovalent ions due to the charged nature. Therefore, water softening is one of the main research focuses for the LBL membranes since their invention by the rejection of either divalent anions like SO_4^{2-} or cations such as Mg^{2+} and Ca^{2+} . The best performed anion and cation separation membranes in the literature were both reported by Bruening's group. The former (Hong et al. 2006) was deposited with $(\text{PSS/PDADMAC})_3\text{PSS}$ on a porous alumina support showed a 96% rejection of SO_4^{2-} , a chloride/sulfate selectivity of 26, and a solution flux of $112.5 \text{ l/m}^2 \text{ h}$ at 4.8 bar. The latter (Ouyang et al. 2008) was deposited with 4 bilayers of PSS/PAH on porous alumina supports with a 95% rejection of MgCl_2 along with a $\text{Na}^+/\text{Mg}^{2+}$ selectivity of 22, and a solution flux of $35.4 \text{ l/m}^2 \text{ h}$ at 4.8 bar. Similar results were obtained in $\text{Na}^+/\text{Ca}^{2+}$ separations. The experiments were performed using mixed feed solutions containing 1 g/L Cl^- and 1 g/L SO_4^{2-} (sodium salts) or 1 g/L Na^+ and 1 g/L Mg^{2+} (chloride salts) respectively. Comparable performance could also be achieved by the similar deposition condition on 50K

commercial PES flat sheet UF membrane substrates (Malaisamy and Bruening 2005; Hong et al. 2006).

2.4. Forward Osmosis

Unlike conventional pressure-driven membrane separation processes such as reverse osmosis (RO) and nanofiltration (NF), the forward osmosis (FO) process utilizes osmotic pressure differences, generated by a high concentration solution (referred to as draw solution) and a low concentration feed stream, as the driving force for the net water transportation across a semi-permeable membrane. The main advantages of this process include: (1) low hydraulic pressure required and thereby low energy consumption compared with the traditional membrane process; (2) the energy can be even harvested through pressure retarded osmosis (PRO) process from the mixing of freshwater and saline water (Gerstandt et al. 2008; Achilli et al. 2009); (3) less fouling tendency and easier for cleaning (Achilli et al. 2009; Mi and Elimelech 2010). Over the last decade, the FO process has shown great potential in various applications including desalination (Choi et al. 2009; Cath et al. 2010), brine concentration (Tang and Ng 2008; Martinetti et al. 2009), waste water treatment (Cornelissen et al. 2008; Lay et al. 2010), and food processing (Jiao et al. 2004; Garcia-Castello et al. 2009).

However, the FO process is still facing several critical challenges to the following aspects: concentration polarization, reverse solute diffusion, draw solution and design of suitable FO membrane. The concentration polarization is due to the concentration difference between the feed solution and the draw solution across the asymmetric FO membrane as shown in Fig. 2-6.

Figure 2-6. Illustration of ICP and ECP in FO process (Zhao et al. 2012).

Normally, the external concentration polarization (ECP) occurs at the surface of dense membrane selective layer which can be mitigated by increased flow turbulence or velocity and optimized water flux (Cath et al. 2006) similar to the pressure-driven process. In contrast, internal concentration polarization (ICP) takes place within the porous support layer of the membrane which cannot be simply controlled by altering hydrodynamic conditions. It is widely accepted that ICP is the major cause for the water flux decline in the FO process (Gray et al. 2006; McCutcheon and Elimelech 2006). Two types of ICP can occur based on the membrane orientations in the FO process. As illustrated in Fig. 2-7, the dilutive ICP can be found when the active layer is facing feed water (AL-facing-FW) as the effective osmotic pressure is reduced by the dilution effect by the permeated feed water with the membrane support layer. On the other hand, the concentrative ICP happens when membrane active layer is facing draw solution (AL-facing-DS) as the effective osmotic pressure is reduced by the accumulated draw solute inside support layer.

Figure 2-7. Illustration of dilutive ICP (a) and concentrative ICP (b) in FO process (Zhao and Zou 2011).

The reverse solute diffusion refers to the diffusion of the solute from draw solution to the feed water through the membrane because of the concentration differences. It is the major contributor of the concentrative ICP and may also enhance membrane fouling (Cath et al. 2006; Hancock and Cath 2009). The specific reverse solute flux is normally used as a measure of membrane selectivity as the ratio of the reverse solute flux to the forward water flux. The membrane with lower specific reverse solute flux is desired with high membrane selective and improved FO efficiency.

Although the selection of the suitable draw solution is also critical for the FO process with three main criteria of high osmotic pressure, ease of re-concentration and/or recovered and minimized ICP in the process (Cath et al. 2006; Zhao and Zou 2011), it is beyond the scope of this thesis and therefore will not be discussed here.

The lack of an adequate membrane is another big hindrances that impede industrial applications of FO. The early studies (Loeb et al. 1997; Cath et al. 2006; McCutcheon and Elimelech 2006) show that commercial RO membranes produce very low water flux in FO operation despite their excellent salt rejection. This lower-than-expected performance is due to the severe internal ICP caused by the thick support layer which greatly reduces the effective osmotic pressure difference across the membrane. Meanwhile, the only available commercial FO membrane

made from cellulose triacetate (CTA) by Hydration Technology Inc (HTI) presents relatively modest performance in various applications because of the high reverse salt flux (McCutcheon and Elimelech 2006; Achilli et al. 2010; Tang et al. 2010).

Extensive efforts have been made by researchers from the membrane community in the fabrication of novel membranes for the FO process with some key design parameters in terms of the water permeability (A), solute permeability (B), membrane structure parameter (S) together with the anti-fouling and anti-ICP properties. Among all, RO-like and NF-like composite membranes with improved structure parameters are the most commonly adopted approaches. In the former approach, membranes are able to effectively reject monovalent ions such as Na^+ and Cl^- when made using the interfacial polymerization technique (Yip et al. 2010; Wei et al. 2011; Chou et al. 2012; Fang et al. 2012). In contrast, the NF-like FO membranes have high rejection of multivalent ions like Mg^{2+} and SO_4^{2-} but relatively low to modest rejection of the monovalent ions. Several types of NF-like FO membranes have been reported such as the integral asymmetric cellulose acetate (CA) membrane by phase inversion (Su et al. 2012), the dual layer polybenzimidazole (PBI) hollow fibers via co-extrusion (Yang et al. 2009) and the poly (amide-imide) (PAI) membrane crosslinked with polyethyleneimine (PEI) (Setiawan et al. 2011; Qiu et al. 2012; Setiawan et al. 2012). The major difference of these two approaches is the choice of draw solutions where NaCl solution is often used for the former and MgCl_2 or Na_2SO_4 are adopted by the latter. A novel dual-skin FO membrane with a combination of RO-like and NF-like skins has also been developed (Fang et al. 2012) with enhanced anti-scaling and anti-ICP properties.

Qiu and Qi were the first group to fabricate NF-like FO membranes using LBL assembly (Qiu et al. 2011; Saren et al. 2011). Up to six bi-layers of PAH/PSS were deposited on partially hydrolyzed polyacrylonitrile (PAN) flat sheet substrate followed by the glutaraldehyde (GA) crosslinking. A water flux of $\sim 60 \text{ L/m}^2\text{h}$ could be achieved by crosslinked xLBL3 membranes in AL-facing-DS orientation using a 0.5 MgCl_2 draw solution and distilled water as the feed water. Cui et al (Cui et al. 2013) also developed LbL membranes made of PAH and a blend of

poly(acrylic acid) (PAA) and PSS on top of hyperbranched PEI modified Torlon substrates and then crosslinked by GA. The 3-bilayer crosslinked membrane has a water flux of 28 L/m²h and reverse salt flux of 1.97 g/m²h using 0.5M MgCl₂ as the draw solution. In the later studies (Liu et al. 2013; Lee et al. 2014), certain nanoparticles such as silica and silver were imbedded in either substrate or polyelectrolyte layers to improve membrane performance. Meanwhile, several researchers have also explored various methods to fabricate RO-like LBL FO membranes using NaCl as the draw solution (Duong et al. 2013; Pardeshi and Mungray 2014; Kwon et al. 2015). Similar to the water softening LBL membrane mentioned in the last section, all of the studies were conducted on the flat sheet membrane substrates. Therefore, it is worthwhile to explore the possibility of applying the LBL deposition technique on a polymeric hollow fiber substrate to make NF composite membranes and evaluate their performance in both water softening and FO processes.

CHAPTER 3 FABRICATION OF LAYER-BY-LAYER ASSEMBLED FORWARD OSMOSIS HOLLOW FIBER MEMBRANES AND THEIR PERFORMANCES USING LOW CONCENTRATION DRAW SOLUTIONS

3.1. Introduction

As mentioned in the literature review, one of the main challenges in the forward osmosis (FO) process is to develop membranes with high performance. The RO-like and NF-like thin film composite (TFC) membranes are among the most popular choices in recent years. The polyelectrolyte layer-by-layer (LBL) assembly is one of the promising techniques to form NF-like composite membranes because of its highly controllable performance and simple procedures for membrane preparation. However, most LBL assembled membranes are in the flat sheet configuration, including the recently reported membranes made by depositing poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonic acid) (PSS) multilayers on a hydrolyzed polyacrylonitrile (PAN) flat sheet substrate for FO application (Saren et al. 2011).

According to the literature (Wang et al. 2010; Xu et al. 2010), hollow fiber membranes possess significant advantages over flat sheet membranes in the FO process due to their high packing density, favorable flow pattern and self-supported structure. Therefore, it is worthwhile to explore the possibility of applying the LBL deposition technique on a polymeric hollow fiber substrate to make NF-like composite membranes and evaluate their performance in the FO process. To the best of our knowledge, such an effort has not been reported previously. In the current work, LBL hollow fibers with different numbers of deposited layers have been fabricated and their FO performance has been tested using deionized (DI) water as the feed and MgCl_2 solutions of various concentrations as the draw solution. Both active layer facing the draw solution (AL-facing-DS) and active layer

facing the feed water (AL-facing-FW) orientations have been tested to explore the potential of the newly developed LBL hollow fibers for FO applications.

3.2. Experimental

3.2.1. Membrane material and chemicals

The polyethersulfone (PES) hollow fiber substrates were produced in-house. PAH (PolyScience, Mw = 120k-200k Da), Poly(ethyleneimine) (PEI, Sigma Aldrich, Mw=750k Da), Poly (diallyldimethylammonium chloride) (PDADMAC, Sigma Aldrich, Mw=100k-200k Da) and PSS (Alfa Aesar, Mw = 500k Da) were used to make polyelectrolyte solutions with sodium chloride (NaCl, Merck) as the supporting electrolyte. The pH of polyelectrolyte solutions was adjusted with diluted hydrochloric acid (HCl) or sodium hydroxide (NaOH) solution. NaCl, sodium sulfate (Na_2SO_4), magnesium sulfate (MgSO_4) and magnesium chloride (MgCl_2) (Merck) were used for NF and FO performance tests. DI water was produced by a Mili-Q system (Milipore,USA).

3.2.2. LBL deposition

The dried hollow fibers were sealed into plastic membrane modules and then immersed into the polyanion PSS and polycation PAH solutions alternately to achieve the desired number of layers. The immersing times for the PSS and PAH solutions were 3 and 5 minutes, respectively, with 3 min DI water rinse in between. The schematic drawing of the deposition process is shown in Figure 3-1. As discussed in section 2.1.2, several deposition conditions including polyelectrolyte type, pH value, supporting electrolyte concentration and the number of deposited layers were investigated by the filtration test using MgCl_2 solution to determine the best combination. Membrane modules were then stored in DI water for NF and FO performance evaluation. Throughout this chapter, one pair of polyelectrolyte (PSS/PAH) deposition is considered as 1 layer of polyelectrolytes and thus n-layer

LBL membrane refers to the membrane with n pairs of (PSS/PAH) deposition (denoted as (PSS/PAH)* n). An n .5-layer LBL membrane signifies a membrane terminated with an additional PSS half-layer on top of the n -layer of polyelectrolytes.

Figure 3-1. Schematic drawing of layer-by-layer deposition on hollow fiber membrane.

3.2.3. Characterization of membrane substrates and LBL membranes

The cross-section structure of the substrate was examined by a Zeiss EVO 50 Scanning Electron Microscope (SEM). The substrate porosity was determined by the gravimetric method, measuring the weight difference between the dry and 2-propanol wetted fibers. The pure water permeability (PWP, using DI water) and molecular weight cut-off (MWCO) tests using a mixed dextran solution were carried out on a bench scale cross-flow filtration unit at 1 bar. The MWCO was then determined by the gel permeation chromatography (GPC, Polymer Laboratories, GPC 50 plus system) (Ren et al. 2006). The dried hollow fiber surface before and after LBL deposition was analyzed by a Fourier transform infra red spectrometer (FTIR, Shimadzu IR Prestige-21) using attenuated total reflection (ATR) method.

3.2.4. Filtration measurement and FO performance tests

The PWP and salt rejection of the LBL hollow fiber membranes were determined by the same cross-flow filtration unit under 1 bar (repeated for three hollow fiber membrane modules). Relatively high cross flow velocity (Reynolds number of around 1500) was maintained for the salt solution flow to minimize the concentration polarization effect. The PWP as well as the salt water permeability (SWP) was calculated as follow:

$$PWP(SWP) = \frac{F}{\Delta P} = \frac{Q}{A\Delta P} \quad (3.1)$$

Where F is the permeation flux ($\text{l/m}^2 \text{ h}$), ΔP is the trans-membrane pressure drop (bar), Q is the volumetric permeation flow rate (l/h), and A is the effective membrane filtration area (m^2)

The salt rejection tests were conducted using a 500 ppm NaCl, Na_2SO_4 , MgSO_4 and MgCl_2 solution, respectively, based on the conductivity measurements (Ultrameter II, Myron L Company, Carlsbad, CA) of the permeate and feed water. The solute rejection including inorganic salt and organic salt mentioned in the later chapter, R (%) was calculated as follows:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (3.2)$$

Where C_f and C_p are the solute concentrations (ppm) in the feed and permeate solutions respectively.

Two FO orientations, the AL-facing-DS and AL-facing-FW, were tested using a lab-scale FO unit which was similar to the unit reported previously (Chou et al. 2010). The Reynolds numbers of the fluids flowing in the lumen and shell side of the modules were kept at around 2000 to minimize external concentration polarization (ECP). MgCl_2 solutions with different concentrations were used as the draw solutions while DI water was used as the feed. The volumetric water flux, J_v , and salt flux, J_s , were measured by the weight and conductivity changes in the feed

tank using a digital mass balance and a conductivity meter connected to a computer logging system. The operation was performed at room temperature of $\sim 23^{\circ}\text{C}$.

3.3. Results and discussion

3.3.1. Determination of optimum deposition conditions

As mentioned in section 2.3, FO membranes with NF-like selective layer require high rejection against multivalent ions with considerable permeation flux. In order to find out the optima deposition conditions for the LBL assembly, several deposition conditions which include polyelectrolyte type, pH value, supporting electrolyte concentration and the number of deposited layers were investigated by the filtration test using MgCl_2 solution.

Poly(styrenesulfonic acid) sodium salt (PSS) and Poly(allylamine hydro-chloride) (PAH) were chosen as the polyelectrolyte pairs to form multilayers for their relatively high charge density to form a tighter multilayer structure with reduced water swelling effect through the higher degree of internal ionic crosslinking; as well as to ensure a sufficient amount of positive charges on the membrane surface. Therefore, much higher Mg^{2+} rejection could be observed as compared to the other two commonly used polycations PEI and PDADMAC in Figure 3-2.

Figure 3-2. Filtration performances of LBL membranes formed with different polycations (deposited with (0.02M PSS with 0.5M NaCl/0.02M polycations with 2.5M NaCl)*2); tested at 1 bar using 500 ppm MgCl₂ solution)

As a weak polyelectrolyte, the effect of pH of PAH solution was also investigated as shown in Figure 3-3. In contrast with Lu's conclusion (Lu et al. 2008), the optimum pH value in this study was about 4.5 which was the origin pH value of the PAH solution. This is quite reasonable as the degree of ionization of PAH solution does not vary too much around pH 2 to 5 (as shown in Figure 2-2) and the molecular weight of PAH used in this experiment was also different from their study (120-200k Da vs. 56k Da). Since the PSS is a strong polyelectrolyte with no pH effect on its ionization, no further pH adjustment was needed for both polyelectrolyte solutions prior to the deposition.

Figure 3-3. Filtration performances of LBL membranes formed with different pH value of PAH solutions (tested at 1 bar using 500 ppm MgCl_2 solution)

The addition of NaCl to the solutions greatly alters the polymer configuration and thus has a major impact on multilayer thickness and charge properties. Different approaches were taken for PSS and PAH solutions respectively. As for the PAH which determined the overall positive charge carried by the membrane, higher salt content was preferred to form the curved polymer structure with excess free charged sites. On the other hand, the amount of salt added into the PSS solution was kept as low as possible to reduce the multilayer thickness and mass transport resistance towards the permeate while maintaining sufficient crosslinking density for the layer stability. The summarized filtration results for both approaches were tabulated in Table 3-1.

Table 3-1. Filtration performances of LBL membranes with different NaCl concentration in polyelectrolyte solutions. ^a

Deposited layers	SWP (l/m ² h bar)	Rejection (%)
Change in supporting electrolyte concentration at poly-anion solution		
(PSS 0.1M NaCl / PAH 2.5 M NaCl)*2	25.4	68.3
(PSS 0.5M NaCl / PAH 2.5M NaCl)*2	13.8	92.5
(PSS 1M NaCl / PAH 2.5M NaCl)*2	10.2	90.5
Change in supporting electrolyte concentration at poly-cation solution		
(PSS 0.5M NaCl / PAH 0.5M NaCl)*2	21.3	67.8
(PSS 0.5M NaCl / PAH 1M NaCl)*2	18.2	80.3
(PSS 0.5M NaCl / PAH 2.5M NaCl)*2	13.8	92.5

^a Tested at 1 bar with 500 ppm MgCl₂ solution

The same filtration tests were performed in order to determine the number of deposited layers. As shown in Table 3-2, a drastic decrease in PWP from 350 to 16.9 l/m² h bar was observed upon completing the first two layers deposition, which indicates the effective coverage of the pores on the substrate surface by the polyelectrolytes. The surface pores were believed to be fully covered after three layers deposition where further increment of the deposition layers only resulted in a slightly drop of the PWP due to increased hydraulic resistance with no significant improvement on the rejection. Therefore, 3-layer LBL membranes (up to 6 layers) were chosen as the starting candidate for the subsequent FO tests with the optimized deposition condition for PSS (0.02M with 0.5M NaCl at a pH around 9) and PAH (0.02M with 2.5M NaCl at a pH around 4) solutions.

Table 3-2. Filtration performances of substrate and LBL membranes.

membrane	Pure water permeability ^a (l/m ² h bar)	Salt water permeability ^a (l/m ² h bar)	MgCl ₂ rejection ^{a,b} %
substrate	350 ± 10	-	-
1-layer	95.4 ± 3.3	74.8 ± 2.5	40 ± 5
2-layer	16.9 ± 0.8	13.8 ± 0.6	92.5 ± 1.5
3-layer	9.6 ± 0.4	7.2 ± 0.2	96 ± 1.2
4-layer	9.4 ± 0.3	7.1 ± 0.3	96.5 ± 1.1
5-layer	7.4 ± 0.2	5.5 ± 0.2	97.8 ± 0.9
6-layer	6.1 ± 0.1	5.1 ± 0.2	97.8 ± 1

^a Tested at 1 bar; ^b MgCl₂ solution concentration is 500 ppm

3.3.2. Properties of membrane substrates and LBL membranes

The cross-section morphology of the PES hollow fiber substrate is shown in Figure 3-4 while its main characteristics are listed in Table 3-3. The substrate used in this study inherited the excellent membrane properties from pervious work (Chou et al. 2010; Wang et al. 2010; Shi et al. 2011) with a further modified pore structure. Some key substrate parameters that were favorable for the FO process including high pure water permeability (350 L/h m² bar), high porosity (84%), a large fiber lumen size (1080 μm) and straight needle-like pores with very thin sponge-like structure (Setiawan et al. 2011; Tiraferri et al. 2011). In addition, the small surface pores with a narrow pore size distribution (mean diameter around 10.9 nm with a standard deviation of 1.04) were beneficial to the subsequent LBL deposition to minimize the polyelectrolytes penetration as well as to increase the deposition homogeneity.

Figure 3-4. Cross-section morphology of PES hollow fiber substrate at 150x.

Table 3-3. Characteristics of PES hollow fiber substrate.

Dimension			Porosity	MWCO	Mean pore size	Standard deviation	Pure water flux	Tensile modulus	Stress at break	Strain at break
OD (μm)	ID (μm)	Thickness (μm)	ε (%)	(kDa)	D* (nm)	σ	(L/h m ² bar)	(Mpa)	(Mpa)	%
1480	1080	200	84	39	10.9	1.04	350	70.4	3.64	66

The FTIR spectra shown in Figure 3-5 confirms the successful deposition of PSS/PAH layers on the substrate surface where the amine bands were detected around 3420 cm^{-1} for -NH_2 group and 2912 cm^{-1} for -NH_3^+ group (Pavia 2009). In addition, a new peak was also observed at 1035 cm^{-1} for the characteristic stretching vibration of the -SO_3 group in PSS (Meier-Haack et al. 2001; Pavia 2009). This was due to the interpenetration nature of the deposited polyelectrolytes even though the terminating layer was PAH in this case (Schonhoff 2003).

Figure 3-5. ATR-FTIR spectra of substrate and 6-layer LBL membrane for (A) indicative peaks of PAH at 3420 cm⁻¹ and 2912 cm⁻¹; (B) indicative peak of PSS at 1035 cm⁻¹.

The rejection mechanism of the 6-layer LBL membrane was determined by performing the filtration test against four types of salt solutions (NaCl, Na₂SO₄, MgSO₄, MgCl₂) as suggested in various studies on NF membranes (Peeters et al. 1998; Schaep et al. 1998). The rejection results are shown in Figure 3-6. It can be seen that the LBL membrane exhibits a high MgCl₂ rejection (above 97%) and a very low Na₂SO₄ rejection (less than 5%), indicating its positively charged nature and that Donnan exclusion played a dominant role in the ion retention at the low salt concentration. In addition to the Donnan effect, the size exclusion also affects the ion rejection in NF. In this experiment, a higher rejection of MgSO₄ than NaCl was observed which probably due to the larger hydrated radii of MgSO₄ as compared to NaCl (0.43nm and 0.38nm for Mg²⁺ and SO₄²⁻ against 0.36nm and 0.33nm for Na⁺ and Cl⁻) (Nightingale 1959). However, the solute rejection of the LBL membrane is expected to be strongly dependent on the surrounding ionic strength. In a high ionic strength environment, the enhanced shielding effect can greatly suppress the Donnan exclusion and thus reduce the salt retention (Teixeira et al. 2005). This is one of the major factors contribute to a distinctive phenomenon observed in the FO performance of NF-like membranes which will be discussed in the next section.

Figure 3-6. Filtration performances of 6-layer LBL membrane with different salt solutions (tested at 1 bar using 500 ppm salt solution)

3.3.3. FO performance in AL-facing-DS orientation

The FO performance of the LBL membranes in terms of water flux (J_v) and the reverse salt flux (J_s) as a function of the deposited layer in AL-facing-DS orientation is plotted in Figure 3-7. A 0.5M MgCl_2 solution was used as the draw solution while the feed was DI water. It was observed that J_v increased from 28 to 40.5 $\text{l/m}^2 \text{h}$ and J_s decreased from 17.15 to 8.1 $\text{g/m}^2 \text{h}$ after 6 layers were deposited. With the increment of the deposited layers, the selective layer thickness increased with the formation of a tighter inter-layer structure due to the polyelectrolyte entanglement (Dubas and Schlenoff 1999). As a result, in the FO process, it established a higher osmotic driving force across the membrane due to the reduced salt leakage, and therefore a higher water flux was obtained. Thus, although the increased number of layers would decrease the water permeability of membrane (Table 3-2) this was more than compensated for by the increase in effective driving

force. Similar trends were observed at various draw solution concentrations ranging from 0.025 to 1 M. One can anticipate better results with a further increment of the deposited layers. However, it is beyond the scope of the current work as it requires a more rigorous deposition protocol to reduce the experimental variations (such as the change of pH and concentration of polyelectrolytes solution) due to the prolonged experiment time (Krogman et al. 2007). Some deposition methods adopted on flat sheet membranes with the aid of automatic instruments can be found elsewhere (Schlenoff and Dubas 2001; Choi and Rubner 2005; Krogman et al. 2007).

Figure 3-7. Effect of deposited layers on FO performance of LBL membrane in AL-facing-DS configuration (□: J_v , ■: J_s) using 0.5 M $MgCl_2$ as draw solution.

The effect of draw solution concentration on a 6-layer LBL membrane is shown in Figure 3-8. Two distinguishable regions of flux increment can be clearly observed at the point around 0.2 M $MgCl_2$ concentration. For charged NF membranes, the salt rejection mechanism is a combination of both Donnan exclusion and size hindrance. As mentioned earlier in section 3.1.1, at a low draw solution concentration, a high salt rejection was expected due to the strong electrostatic repulsion of the selective layer to the co-ions of Mg^{2+} . Thus, the water flux

increased almost linearly with increased osmotic pressure within the first region (from 8.6 l/m² h at 0.025 M to 30.2 l/m² h at 0.2 M). In the second region, however, the shielding effect on the membrane surface charges caused by the counter-ions of Cl⁻ became more severe with an elevated draw solution concentration as the selective layer was exposed to the draw solution directly. Therefore, the Donnan exclusion was greatly suppressed, resulting in a significant salt leakage to the feed water. It not only reduced the osmotic pressure difference across the selective layer but also enhanced the concentrative internal concentration polarization (ICP) (Gray et al. 2006) inside the porous substrate, which further reduced the effective osmotic driving force. Consequently, when the concentration of the draw solution increased from 0.5 to 1 M, there was only a marginal increase of water flux (from 40.5 l/m² h to 41 l/m² h) but with a high reverse salt flux (13.47 g/m² h).

Figure 3-8. FO performance of LBL membrane in AL-facing-DS configuration ($\square$: J_v , $\blacksquare$: J_s) with effect of draw solution concentration on 6-layer LBL membrane.

3.3.4. FO performance in AL-facing-FW orientation

Figure 3-9 illustrates the FO performance of the LBL membrane in AL-facing-FW orientation. From Figure 3-9 it can be seen that the effect of deposited layers on J_v and J_s in this orientation is not as pronounced as in AL-facing-DS orientation (Figure 3-7). When the porous substrate was placed against the draw solution, the dilutive ICP took place in the membrane substrate where the salt concentration at the interior surface of the selective layer was greatly diluted by the convective water flow from the feed side (Gray et al. 2006). Thus, the actual salt concentration at the charged membrane surface was much lower than the bulk solution, leading to a much less shielding effect. Since the degree of the dilutive ICP is mainly determined by the substrate structure, the salt rejection did not vary too much with the increase in the number of deposition layers under the same draw solution concentration.

Figure 3-9. Effect of deposited layers on FO performance of LBL membrane in AL-facing-FW configuration ($\square: J_v, \blacksquare: J_s$) using 0.5 M MgCl_2 as draw solution concentration.

The dilutive ICP also resulted in a better salt rejection at a high draw solution concentration for the 6-layer LBL membrane in the AL-facing-FW orientation. As shown in Figure 3-10, the salt flux was only 4.1 g/ m² h using a 2 M draw solution

compared with 13.47 g/ m² h at 1 M in the AL-facing-DS orientation. As a trade off, the water flux was also much lower (25.63 l/m² h) than the previous case due to the smaller effective osmotic gradient across the selective layer.

Figure 3-10. FO performance of LBL membrane in AL-facing-FW configuration (□: J_v , ■ J_s) with effect of draw solution concentration on 6-layer LBL membrane.

3.3.5. Comparison with other NF-like membranes

Table 3-4 lists the FO performance of the 6-layer LBL hollow fibers along with some NF-like FO membranes from the literature. It can be seen that the LBL hollow fibers exhibited superior performance in both orientations for its high water flux and low salt leakage compared with others under the same test conditions. In particular, reasonably high water fluxes of 14.6 and 25.9 l/m² h with corresponding low J_s/J_v ratios of 0.034 and 0.066 g/L can be achieved using 0.05 and 0.1 M draw solution concentrations, respectively, in the AL-facing-DS orientations. These promising results indicate the possibility of substantial reductions of the draw solution replenishment, and the energy consumption for draw solution regeneration and separation using LBL hollow fiber FO membranes.

Table 3-4. Comparison of various NF-like membranes in FO process.

Sample	Water flux (l/m ² h)	Salt flux/water flux (g/l)	Draw solution	Feed	Orientation	Reference
6-layer LBL membrane	14.6	0.034	0.05 M MgCl ₂	DI water	AL-facing-DS	Present work
	25.9	0.066	0.1 M MgCl ₂	DI water	AL-facing-DS	Present work
	40.5	0.201	0.5 M MgCl ₂	DI water	AL-facing-DS	Present work
CA double-skinned hollow fiber	15.7	0.06	0.5 M MgCl ₂	DI water	AL-facing-DS	(Su, Chung et al. 2012)
PAI-PEI crosslinked hollow fiber	13.13	0.7	0.5 M MgCl ₂	DI water	AL-facing-DS	(Setiawan, Wang et al. 2011)
LBL flat sheet	25.1	0.568	1.0 M MgCl ₂	DI water	AL-facing-DS	(Saren, Qiu et al. 2011)
Dual-layer hollow fiber	PBI 15.6	0.038	2.0 M MgCl ₂	DI water	AL-facing-DS	(Yang, Wang et al. 2009)
6-layer LBL membrane	18.44	0.113	0.5 M MgCl ₂	DI water	AL-facing-FW	Present work
	20.66	0.138	1.0 M MgCl ₂	DI water	AL-facing-FW	Present work
PAI-PEI crosslinked hollow fiber	8.36	0.3	0.5 M MgCl ₂	DI water	AL-facing-FW	(Setiawan, Wang et al. 2011)
LBL flat sheet	22	0.302	1.0 M MgCl ₂	DI water	AL-facing-FW	(Saren, Qiu et al. 2011)
Dual-layer hollow fiber	PBI 7.5	0.053	2.0 M MgCl ₂	DI water	AL-facing-FW	(Yang, Wang et al. 2009)

3.4. Conclusions

The layer-by-layer polyelectrolyte deposition technique has been successfully applied on a PES hollow fiber substrate to make novel LBL hollow fibers for FO application for the first time. A simple deposition procedure involves immersing the substrate into the polyanion PSS and polycation PAH solutions alternately to achieve the desired number of deposition layers.

The newly developed LBL hollow fibers exhibited excellent FO performance. With 6 layers of polyelectrolyte deposited, the membrane showed a high water flux of 40.5 l/m² h with a low J_s/J_v ratio of 0.201 g/L when using DI water as the feed and a 0.5 M MgCl₂ solution as the draw solutions in the AL-facing-DS orientation. In

addition, 14.6 and 25.9 l/m² h water fluxes with corresponding low J_s/J_v ratios of 0.034 and 0.066 g/L can be achieved using 0.05 and 0.1 M MgCl₂ draw solution concentrations, respectively, in the same orientation, suggesting great potential of the LBL hollow fibers in the FO process. They should be able to substantially reduce the draw solution replenishment, and the energy consumption for draw solution regeneration and separation.

CHAPTER 4 ENHANCED HOLLOW FIBER MEMBRANE PERFORMANCE VIA SEMI- DYNAMIC LAYER-BY-LAYER POLYELECTROLYTE INNER SURFACE DEPOSITION FOR NANOFILTRATION AND FORWARD OSMOSIS APPLICATIONS

4.1. Introduction

In chapter 3, a new type of layer-by-layer polyelectrolyte deposited hollow fiber membrane was developed for forward osmosis application. However, due to its relatively large fiber dimension and porous thin-wall structure, it was not robust enough to be used in pressure-driven processes in outside-in configuration even at low operating pressure (2-5 bars).

Based on our groups' past experience of interfacial polymerization on the inner surface of various hollow fiber UF membrane substrates (Chou et al. 2012; Fang et al. 2012), it is proved that the inner surface modification may possess several advantages over the shell side: (1) the lumen surface of the hollow fiber substrate is better protected during the membrane spinning, handling and storage process; (2) the confined space inside the substrate lumen enhances the homogeneity and controllability of the chemical modification and significantly reduces the chemical requirement; (3) it can minimize the experimental uncertainty caused by air bubbles, membrane overlapping, etc., that are often encountered during outer surface modification; and (4) the thin-wall structured membrane can withstand much higher operating pressure from the lumen surface which is more preferable in the pressure-driven process.

A few research groups have also investigated the possibility of applying LBL deposition on the inner surface of a hollow fiber substrate. However, those studies were only limited to the prevaporation (Su et al. 2012) and catalytic (Ouyang et al. 2010) applications. Therefore, in this study inner skin deposited LBL membranes

were fabricated for nanofiltration (NF) and forward osmosis (FO) applications. A semi-dynamic process was adopted which involved the dynamic introduction/replacement of solutions into the fiber lumen by syringes followed by the static contacts for a desired time. The developed membranes were characterized by a series of standard protocols, and then tested in NF and FO processes. Their performances were also compared with previous studies to confirm the superiority of the inner deposition LBL method.

4.2. Experimental

4.2.1. Materials

The same polyethersulfone (PES) hollow fiber substrates were used as in Chapter 3. Poly(allylamine hydrochloride) (PAH, PolyScience, $M_w = 120\text{k-}200\text{k Da}$), Poly(ethyleneimine) (PEI, Sigma Aldrich, $M_w = 750\text{ kDa}$), Poly(diallyldimethylammonium chloride) (PDADMAC, Sigma Aldrich, $M_w = 100\text{-}200\text{ kDa}$) and poly(styrenesulfonic acid) sodium salt (PSS, Alfa Aesar, $M_w = 500\text{ kDa}$) were used to make polyelectrolyte solutions with sodium chloride (NaCl, Merck) as the supporting electrolyte. The molecular structures and functional groups of the above mentioned polyelectrolytes can be found in Table 4-1. NaCl, calcium chloride (CaCl_2) and magnesium chloride (MgCl_2) (Merck) were used for NF and FO performance tests. Neutral organic solutes such as glucose, sucrose and raffinose were purchased from Merck and used to determine LBL membrane molecular weight cut-off (MWCO). Hydrochloric acid (HCl fuming 37%) and sodium hydroxide (NaOH) obtained from Merck were used to adjust membrane storage water for acid/ alkaline stability test. DI water was produced by a Mili-Q system (Milipore, USA)

Table 4-1. Polyelectrolyte structure and functional groups.

Name	Molecular Structure	Functional Groups
Poly(styrene sulfonate) PSS		SO_3^-
Poly(allylamine hydrochloride) PAH		NH_3^+
Poly(diallyl-dimethylammonium chloride) PDADMAC		NR_4^+
Poly(ethyleneimine) PEI		NH_3^+ NRH^{2+} NR_2H^+

4.2.2. Inner surface layer-by-layer deposition

The dried hollow fibers were sealed into plastic membrane modules with an effective length of 24 cm. The LBL deposition at the lumen surface of the substrate was performed by introducing the polyelectrolyte solution throughout the fiber lumen with a syringe and maintained for a desired contact time. In contrast with other inner deposition methods mentioned in section 2.2.3, no peristaltic or vacuum pumps were required in the process with significantly reduced chemical consumption. The schematic drawing of the deposition process is shown in Fig.4-1. The polyanion PSS and polycation PAH, PDADMAC, PEI solutions were prepared following the optimized formula discussed in the Chapter 3 and applied alternately to achieve the desired number of layers. The contact times for the hollow fiber with PSS and different polycation solutions were 3 and 5 minutes, respectively, with a 3-minute DI water rinse in between. Membrane modules were then stored in DI water for NF and FO performance evaluation. For a comparison purpose, the outer deposited LBL membrane was also fabricated following the same protocol as in the last chapter and tested in NF application. Throughout this chapter, the id-LBL and

od-LBL refer to inner surface deposited and outer surface deposited LBL membranes respectively; one pair of polyanion (PSS)/polycation (PAH) deposition is considered as one layer of polyelectrolytes and thus LBL-xI(O) refers to the membrane with x pairs of (PSS/PAH) inner(outside) deposition.

Figure 4-1. Schematic drawing of layer-by-layer deposition on hollow fiber inner surface.

4.2.3. Membrane characterization

The morphology of the substrate and LBL membranes were examined by a Field Emission Scanning Electron Microscope (FE-SEM JSM-7600F, JEOL, Japan). The surface charge properties of these membranes were determined by zeta potential method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) with an electrolyte solution of 0.01M potassium chloride (KCl). The hollow fiber membrane samples were flattened (the fibers were cut opened for the inner surface measurement) and mounted oppositely on the rectangular holders facing the streaming channel. The streaming currents were measured and converted to the zeta potential results by its built-in software using Helmholtz-Smoluchowski equation:

$$\zeta = \frac{dI_{str}}{d\Delta p} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{L}{A} \quad (4.1)$$

where the measured streaming current coefficient $dI_{str}/d\Delta p$ is related to the cell constant L/A of the streaming channel. L is the length of the rectangular slit channel between the holders and A is the cross-section area. η and $\varepsilon \times \varepsilon_0$ are the viscosity and dielectric coefficient of the electrolyte solution.

The molecular weight cut-off (MWCO), i.e., the molecular weight of the solute with 90% rejection, of the LBL membranes were measured on a bench scale cross-flow filtration unit at 1 bar using a 200 ppm solution of glucose, sucrose and raffinose respectively. The rejection of neutral organic solutes was obtained from the concentration of the feed and permeate solutions based on the total organic carbon measurements using a TOC analyzer (TOC-VCSH, Shimadzu, Japan). The effective pore size of the NF membrane was estimated using the Donnan-Steric-Pore model (DSPM). Based on the model, the rejection to neutral organic solutes is given by (Bowen et al. 1997; Bowen and Mohammad 1998):

$$R = (1 - \Phi K_{i,c}) \times 100\% \quad (4.2)$$

Where

$$\Phi = (1 - \lambda^2) \quad (4.3)$$

$$K_{i,c} = (2 - \Phi)(1.0 + 0.054\lambda - 0.988\lambda^2 + 0.441\lambda^3) \quad (4.4)$$

Φ is the steric partitioning factor, $K_{i,c}$ is the steric hindrance factor, and λ is the ratio of solute radius to effective pore radius. Since the solute rejection is only related to λ , the effective pore radius of the membrane can be obtained based on the rejection to various solutes by knowing their solute radii through the following empirical equation (Bowen and Mohammad 1998):

$$\log r_s = -1.3363 + 0.395 \log M_w \quad (4.5)$$

where r_s is the Stocks radius of a neutral solute molecule (nm), and M_w is the molecular weight of the solute (Da).

4.2.4. NF and FO performance tests

The salt water permeability and salt rejection of the LBL hollow fiber membranes were determined by the same cross-flow filtration unit under 2 bar pressure

(repeated for three hollow fiber membrane modules). A relatively high cross flow velocity (0.5m/s) was maintained for the salt solution flow to minimize the concentration polarization effect. The salt solutions were always facing the membrane active layer where the inside-out filtration was performed for id-LBL membranes and vice versa. The single salt rejection tests were conducted using a 1000 ppm MgCl_2 solution, based on the conductivity measurements (Ultrameter II, Myron L Company, Canada) of the permeate and feed water. For 3000 and 5000 ppm mixed salt tests, cation concentrations in the feed and permeate solutions were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer, USA). In addition, various membrane stability tests including acid/alkaline, high shear flow and back wash tests were also performed using the same filtration unit. The FO tests in this study followed the same protocol as discussed in details in last chapter.

4.3. Results and discussion

4.3.1. Characteristics of LBL hollow fibers

The characteristics of the PES membrane substrate and both outer and inner surface deposited LBL hollow fibers are studied and compared in this section including surface morphology, charge properties as well as the MWCO of the membranes.

The FE-SEM images of membrane surface before and after LBL deposition are shown in Fig.4-2. Visible pores existed on both outer (Fig.4-2 (a)) and inner surface (Fig.4-2 (c)) of PES substrates. The smooth surface with patterned structure was observed on the fiber lumen which might be related to the vertical stretching force during the spinning process. In contrast, the outer surface seems to be rougher with irregular topography which may cause an uneven distribution of the deposited layer. Nevertheless, upon two layer LBL deposition, the surface pores were fully covered by the polyelectrolyte multilayer on both surfaces (Fig.4-2 (b, d)) with some possible polymer aggregates.

Figure 4-2. FESEM images of substrate (a) outer surface; (b) od-LBL membrane outer surface; (c) substrate inner surface; (d) id-LBL membrane inner surface at magnification of 100k. (Deposited with (PSS with 0.5 M NaCl/PAH with 2.5 M NaCl) x 2)

The surface charge properties of the substrate and the LBL membranes are presented in Fig. 4-3. The PES substrate possesses slightly negative surface charge throughout the tested pH range (auto-titrated from pH 10 to 4). On the other hand, the iso-electric points for both the od-LBL and id-LBL membranes are around pH 8 which suggests that these membranes are positively charged below this pH value since the polycation PAH were used as the capping layer. Moreover, the higher zeta potential readings of the id-LBL membrane indicate its higher surface charge density than the outer deposited one.

Figure 4-3. Zeta potential of PES substrate and LBL membranes
(Deposited with (PSS with 0.5 M NaCl/PAH with 2.5 M NaCl) x 2).

The rejection of the NF membranes towards the neutral solute exclusively depends on the size-based selectivity by eliminating the Donnan effect and is often used to estimate the MWCO and the effective pore size of the NF membrane (Bowen and Mohammad 1998; Boussu et al. 2006). The properties of the three neutral solutes, glucose, sucrose and raffinose, are listed in Table 3 together with their rejections by both od-LBL and id-LBL membranes. The Stokes radius of the solutes were calculated using the empirical equation based on their molecular weight (Bowen and Mohammad 1998). It can be seen that the MWCO of the od-LBL and id-LBL membranes were around 855 Da and 296 Da, respectively, by plotting their rejections against solute molecular weights. The mean value of the effective pore radius for those membranes were about 0.95 nm and 0.6 nm, respectively, estimated by the Donnan-steric-Pore (DSPM) model (Bowen and Mohammad 1998). It seems that both membranes' pore sizes are within the range of NF membrane, but the inner deposition could achieve a much tightened pore structure than the outer deposition.

Table 4-2. Neutral solutes rejection performance.

Solute	Molecular weight (Da)	Stokes radius (nm)	LBL-2O	LBL-2I
			Solute rejection (%) ⁻	Solute rejection (%) ⁺
Glucose	180	0.359	38.2 ± 3.2	69.8 ± 1.2
Sucrose	342	0.462	67.2 ± 4.5	98.1 ± 0.5
Raffinose	504	0.538	74.4 ± 4.7	98.3 ± 0.5

⁺Tested at 1 bar using 200 ppm neutral solute solutions

4.3.2. Single salt rejection tests

Three polycations, PAH, PEI and PDADMAC, were used to form id-LBL membranes and tested with a 1000 ppm MgCl₂ solution under 2 bar pressure. The results are plotted and compared with outer deposited membranes in Fig. 4-4. It is clearly shown that the rejection for all inner deposited membranes were improved with a noticeable 100% increment of PDADMAC membrane, which was considered to be not capable for multivalent cation rejection in previous studies (Ouyang et al. 2008; Rajabzadeh et al. 2014). Since the NF rejection is governed by both Donnan effect and size hindrance, the better rejection could probably be due to a more effective selective layer with higher surface charge density and smaller pore sizes produced by the inner deposition, evidenced by the characterization results in Section 4.3.1. Among all, the PAH id-LBL membrane had the best rejection performance with a salt water permeability (SWP) of 9.8 l/m² h bar and an over 98% Mg²⁺ rejection. Therefore, only PAH deposited membranes were used for further study.

Figure 4-4. Nanofiltration performance of LBL membranes using different polycations.
(Deposited with (PSS with 0.5 M NaCl/Polycations with 2.5 M NaCl) x 2; tested at 2 bar using 1000 ppm MgCl₂ solution)

The LBL membranes were then challenged with an elevated salt concentration (4000 ppm MgCl₂ solution) at a higher operating pressure (4.8 bar). The od-LBL membrane was squashed quickly in the outside-in filtration configuration under this pressure. However, the id-LBL membrane could still maintain excellent performance (SWP of 8 l/m² h bar and rejection of 97%) up to 8 hours of testing time. It suggests that the id-LBL membrane can withstand higher operating pressures and thus is more suitable for the NF application.

In Table 4-3, the NF performance of the id-LBL membrane is compared with commercial NF membranes (Schaepe et al. 1998; Ouyang et al. 2008), the best LBL membrane for cation separation reported previously (Ouyang et al. 2008) and some other chemically modified positively charged NF membranes (Ba et al. 2009; Chiang et al. 2009; Ji et al. 2011). Among all, the id-LBL membrane shows superior performance in terms of both water flux and MgCl₂ rejection. Only the positively charged commercial UTC-20 membrane has the comparable performance but it requires a considerably higher operating pressure of 10 bar.

Table 4-3. Comparison of various NF membranes.

Membranes	Salt water permeability (l/m ² h bar)	Salt rejection (%)	MgCl ₂ concentration (ppm)	Operation pressure (bar)	Reference
LBL-2I	9.8	98.2	1000	2	Present work
	8.2	97.4	4000	4.8	Present work
LBL-6O	12	94	1000	2	Chapter 3
UTC-20	9.7	98	1500	10	(Schaepe et al. 1998)
NF-270	4	53	4000	4.8	(Ouyang et al. 2008)
LBL flat sheet	4	93	4000	4.8	(Ouyang et al. 2008)
PDMAEMA/Psf	1	98	1000	8	(Ba et al. 2009)
PEI/TMC IP	9.75	80	1000	4	(Chiang et al. 2009)
PDMCHEAs/Psf	3.2	94.3	1000	6	(Ji et al. 2011)

4.3.3. Mixed salt rejection tests

The performance enhancement of the id-LBL membrane was more pronounced over the outer deposited ones in the mixed salt solution tests. In Table 4-4, the cation compositions of the 3000 and 5000 ppm TDS feed solutions are listed with the rejection performance of both membranes. It is known that rejection ability of the NF membranes is greatly influenced by the ionic strength of the feed solution. With increased counter-ion concentration, the membrane rejection based on the Donnan exclusion is weakened due to the screening effect while the steric hindrance gradually plays a more important role. In the experiments, it is obvious that the od-LBL membranes cannot effectively reject Mg²⁺ and Ca²⁺ when tested with a 5000 ppm TDS solution, while the id-LBL membranes could still maintain more than 90% rejection for both of them. This was also due to the higher surface charges carried by the id-LBL membrane in combination with smaller surface pores shown earlier on. Nevertheless, in all the cases, Na⁺ rejection was much lower than that of Mg²⁺ and Ca²⁺ due to the co-ions competition where Na⁺ was easier to pass through the membrane with less charges and higher mobility (Luo and Wan 2013). This is one of the crucial features for good NF membranes that the selective passage of

monovalent co-ions could effectively reduce the osmotic pressure difference in the water softening process. However, the operating pressure still needs to be adjusted accordingly to overcome the elevated osmotic pressure due to the divalent ions in the feed solution. Otherwise, as shown in the last two rows (operated at 2 and 4.8 bar) of Table 5, both water permeability and ion rejection of the membrane would decline due to the lack of sufficient driving force.

Table 4-4. Separation performance of mixed salt solutions.

Feed solution TDS (ppm)	Ion composition (ppm)			Membrane ^a	SWP ^b (l/m ² h bar)	Ionic rejection (%)		
	Mg ²⁺	Ca ²⁺	Na ⁺			Mg ²⁺	Ca ²⁺	Na ⁺
3000	142	266	562	od-LBL	11	91	87	11
				id-LBL	8.1	99.5	99	13.7
5000	218	420	894	od-LBL	7.2	72.5	68.8	-7.1
				id-LBL (2 bar)	4.8	96.2	92.1	7.6
				id-LBL (4.8 bar)	7.4	99.6	97	16.4

^a Deposited with (PSS with 0.5 M NaCl/PAH with 2.5 M NaCl) x 2

^b Tested at 2 bar unless indicated in the table

4.3.4. Membrane stability tests

The id-LBL membranes were stored in either pH 2 or pH 12 solutions for 14 days to test their chemical stability. The pH value of the solutions was adjusted after each filtration test and the membrane lumens were refilled with the solution by a syringe. From the repeated test results shown in Figure 4-5, only slightly flux drop with no rejection deterioration was observed during the testing period.

Figure 4-5. 14-day acid/alkaline stability tests of inner deposited LBL membranes (Deposited with (PSS with 0.5 M NaCl/PAH with 2.5 M NaCl) x 2).

In addition, the mechanical strength (selective layer binding stability) of the id-LBL membrane were tested by 8 hours of high shear flow (6 times higher than the normal operation at 3.2 m/s) and 8 hours of back flush by DI water at 2 bar subsequently. Similarly, no noticeable flux and rejection drop of the tested membranes were obtained upon stability tests. Therefore, it can be concluded that the id-LBL membrane possess superior chemical and mechanical stability with great potential in future practical applications.

4.3.5. Forward osmosis performance tests

In Chapter 3, the six-layer od-LBL membrane was studied in FO process with considerable high water flux and low salt leakage by using low concentration MgCl_2 draw solutions. Encouraged by the remarkable NF performance improvement by switching to inner surface deposition, the id-LBL membranes were also tested in FO experiments for both active layer facing draw solution (AL-facing-DS) and active layer facing feed water (AL-facing-FW) orientations. As expected, with only two layer deposition, the id-LBL membrane demonstrated greater competency in terms of both improved water flux and reduced salt leakage.

Figure 4-6. FO performance of LBL membranes using up to 1 M MgCl_2 draw solutions. (A) Water flux; (B) salt flux/water flux.
 (od-LBL membranes deposited with (PSS/PAH)*6 (Chapter 3); id-LBL membranes deposited with (PSS/PAH)*2)

In the AL-facing-DS configuration, a remarkable flux (J_v) increment (about 80% increase from ■ to □ data sets) was achieved for the id-LBL membranes in all tested draw solution concentrations as shown in Fig. 4-6(A). By comparing the salt flux over water flux (J_s/J_v) data in Fig. 4-6(B), it can be seen that because of the better MgCl_2 rejection, the id-LBL membrane was able to unitize the osmotic

driving force from the draw solution more efficiently and thus could achieve higher flux than the od-LBL membranes.

However, the flux increment was not so obvious in the AL-facing-FW configuration with only about 20% increase from ● to ○ data sets. This was due to the dilutive internal concentration polarization which greatly reduced the effective osmotic pressure in this configuration. Similar observations had been discussed in details in chapter 3. Nevertheless, the id-LBL membrane still produced the lowest J_s/J_v value with only around 0.03 g/L using 0.5 M $MgCl_2$ draw solution, as compared with reported data in the literature.

Table 4-5. Comparison of various LBL FO membranes.

Sample	Water flux (L/m ² h)	Salt flux/water flux(g/l)	Orientation	Reference
LBL-2I	73	0.06	AL-facing-DS	Present work
LBL-6O	40.5	0.2	AL-facing-DS	Chapter 3
6#LBL FO	22 ^a	0.3 ^a	AL-facing-DS	(Saren et al. 2011)
(PAA-PSS/PAH) ₃	28	0.07	AL-facing-DS	(Cui et al. 2013)
xLbL3	60 ^a	0.1 ^a	AL-facing-DS	(Qiu et al. 2011)
(PAH/PSS) _{3XX}	21	0.06	AL-facing-DS	(Duong et al. 2013)
LBL-2I	21.5	0.03	AL-facing-FW	Present work
LBL-6O	18.4	0.11	AL-facing-FW	Chapter 3
6#LBL FO	16 ^a	0.57 ^a	AL-facing-FW	(Saren et al. 2011)
xLbL3	30 ^a	0.3 ^a	AL-facing-FW	(Qiu et al. 2011)
(PAH/PSS) _{3XX}	14.5	0.08	AL-facing-FW	(Duong et al. 2013)

Feed solution: DI water; draw solution: 0.5M $MgCl_2$ solution

^a Estimated from published figures

In Table 4-5, the FO performance of the id-LBL membrane using 0.5M $MgCl_2$ draw solution with DI water as feed solution is compared with other polyelectrolyte LBL FO membranes (Saren et al. 2011; Cui et al. 2013) with glutaraldehyde (Qiu et al.

2011) and UV crosslinking (Duong et al. 2013). Despite the fewest modification steps involved, the id-LBL membrane was able to achieve the highest water flux with lowest reverse salt flux among all.

4.4. Conclusions

The LBL polyelectrolyte deposition was successfully applied on the inner surface of the PES hollow fiber substrate to form composite NF membrane. The deposition was carried out in a semi-dynamic process with the aid of syringes. The developed membranes were then characterized and tested in NF and FO applications and the performance were compared with our previous studies using outer surface deposition and literature data.

It is found that the id-LBL membranes were more suitable for NF application than the outer deposited ones, not only because they could withstand higher operating pressure, but also possess superior hardness rejection especially in high concentration mixed salt solutions. As for the FO process, with only two layer deposition, the id-LBL membranes also demonstrated significant performance improvement with increased water flux and reduced salt leakage. Therefore, it can be concluded that for the hollow fiber substrate, the inner surface is more suitable for LBL deposition than the outer surface. In further experiments, the deposition formula will be further optimized to enhance the water permeability. The feasibility for the pilot scale study will also be explored.

CHAPTER 5 CROSSLINKED LAYER-BY-LAYER HOLLOW FIBER MEMBRANE FOR LOW- PRESSURE WATER SOFTENING

5.1. Introduction

In typical hard water, a significant amount of multivalent counter-ions, normally the SO_4^{2-} , are presented ranging from 100 ppm (ground water) to 2500 (seawater) ppm (Song et al. 2011; Galanakis et al. 2012). During the membrane softening process, those counter-ions can be absorbed on the membrane surface to partially neutralize the membrane charge or even to cause the charge inversion (Schaep et al. 1999; Garcia-Aleman and Dickson 2004). On the other hand, for feed water with relatively high salinity, the shielding effect can also greatly reduce the electrostatic repulsion of the divalent ions by the charged membranes. Therefore, size exclusion is expected to play a more important role due to the weakened charge effect. However, most of previous studies only focused on the membrane charge properties and considered the MgCl_2 rejection or $\text{Mg}^{2+}/\text{Na}^+$ selection ratio in the common counter-ion (Cl^-) mixed salt system as the performance indicators for water softening which were too simplified to reveal the membrane intrinsic separation properties for the real process.

In Chapter 4, a positively charged nanofiltration (NF) membrane was prepared via inner surface layer-by-layer (LBL) polyelectrolyte deposition with superior divalent cation rejection and high water flux. However, it was later found that the membrane rejection was drastically deteriorated in the presence of SO_4^{2-} in the feed water. As discussed earlier on, the size exclusion is expected to play a more important role due to the weakened charge effect in this situation. Thus the LBL membranes need further modification to enhance their water softening performance of synthesized hard water in the presence of divalent counter ion SO_4^{2-} .

Glutaraldehyde (GA) crosslinking was adopted by many researchers to enhance the sieving ability of various polymeric NF membranes previously (Musale and Kumar 2000; Musale and Kumar 2000; Qiu et al. 2011; Zheng et al. 2013). During the

crosslinking, the aldehyde groups of the GA molecule react with amine groups on the membrane surface to form the Schiff base ($-C=N-$). Upon successful reaction, the molecular weight cut off (MWCO) and permeability of the membrane was reduced while the retention of certain neutral solutes and inorganic salts were generally increased. Zheng et al. (Zheng et al. 2013) fabricated a positively charged composite membrane with a MWCO of 650 Da by GA crosslinking of polyvinyl alcohol (PVA) and polyquaternium-10 coated polypropylene hollow fibers for the removal of cationic dyes through submerged filtration. Qiu et al. (Qiu et al. 2011) greatly improved the forward osmosis performance of a LBL assembled poly(acrylonitrile) (PAN) membrane by the GA crosslink of Poly(allylamine hydrochloride) (PAH) with enhanced $MgCl_2$ rejection. Musale and Kumar (Musale and Kumar 2000) studied the surface crosslinking effect of different GA concentrations and crosslinking time on the surface chemical composition and sieving properties of chitosan/PAN composite NF membranes and managed to reduce the membrane MWCO from >1500 Da to 550-700 Da. Meanwhile, another work from the same group (Musale and Kumar 2000) suggested the GA crosslinking could also significantly increase the membrane solvent and pH resistance by decreased pore size and swelling effect.

In this study, GA crosslinking was adopted in a combination of modified LBL polyelectrolyte deposition conditions to develop a novel hollow fiber NF membrane with low-pressure water softening capability for synthesized hard water containing divalent counter ion SO_4^{2-} . The challenges for the new membrane include (a) the presence of SO_4^{2-} in the feed water, which tends to deteriorate positively charged NF membrane retention of divalent ions; (b) high salinity feed water up to 10,000 ppm total dissolved salt (TDS); (c) 2 bar operating pressure that requires the membrane to have a good Mg^{2+}/Na^+ selectivity and less mass transfer resistance in the substrate; and (d) better separation performance as compared with the state-of-the-art and commercial NF membranes. The characteristics of the newly developed membranes were studied thoroughly and compared with uncrosslinked LBL membranes. In addition, NF 90 and NF 270, as the representatives of the “loose” and “tight” type commercial membranes (Schaep et al. 2001; Nghiem et al. 2005), were also tested for their water softening capability for comparison.

5.2. Experimental

5.2.1. Materials

The same polyethersulfone (PES) hollow fiber substrates were used as in Chapter 3. The inner and outer diameters of the substrate are 1.0 and 1.4 mm, respectively, with the pure water permeability of around 350 l/m² h bar and the MWCO of 50 kDa. PAH (Sigma Aldrich, Mw=15 kDa), and poly(styrenesulfonic acid) sodium salt (PSS, Alfa Aesar, Mw = 500 kDa) were used to make polyelectrolyte solutions with sodium chloride (NaCl, Merck) as the supporting electrolyte. Glutaraldehyde solution (GA, 50% in water) was obtained from Sigma Aldrich as the crosslinking agent. NaCl, calcium chloride (CaCl₂), sodium sulfate (Na₂SO₄), magnesium sulfate (MgSO₄) and magnesium chloride (MgCl₂) (Merck) were used for NF performance tests. Neutral organic solutes such as glycerol, glucose and sucrose were purchased from Merck and used to determine the MWCO of NF membranes. DI water was produced by a Mili-Q system (Milipore, USA).

5.2.2. Layer-by-layer deposition and crosslinking

The detailed procedures of the semi-dynamic inner surface modification were reported in Chapter 4 and briefly discussed below. The dried hollow fibers were sealed into PTFE membrane modules with an effective length of 24 cm. The LBL deposition and GA crosslinking at the lumen surface were performed by introducing the polyelectrolyte and the GA solutions throughout the fiber lumen with a syringe and maintained for a desired contact time followed by DI water rinse after each step. The deposition parameters such as the molecular weight and concentration of the polyelectrolyte, supporting electrolyte (NaCl) concentration and the crosslinking conditions were examined to optimize the membrane performance. The optimized modification parameters are summarized and presented in Table 5-1. Membrane modules were then stored in DI water for characterization and performance evaluation. Throughout this chapter, the membrane deposited with n pairs of

(PSS/PAH) deposition is termed as LBL*n membrane while the crosslinked ones are referred as LBL*nC membrane.

Table 5-1. Optimized membrane modification parameters.

Solution	Concentration	Supporting electrolyte concentration (M)	pH	Contact time (minutes)
PSS	0.02 M	0.5	9	3
PAH	0.1 M	0.5	4	5
GA	0.1% (wt)	-	5	8

5.2.3. Characterization of hollow fibers

All surface characterizations of the hollow fibers were conducted on the membrane inner surface by cutting open the fibers and carefully placed onto the respective holders.

The morphology of the NF membrane was examined by a Field Emission Scanning Electron Microscope (FE-SEM JSM-7600F, JEOL, Japan). The surface elemental analysis of the membrane was carried out using the VG ESCALab 220i-XL Imaging XPS. Mg K α X-ray ($h\nu=1253.6\text{eV}$) from twin anode X-ray gun was employed using a small area 150 (SA150) lens mode for analysis with photoelectron take-off angle of 90° with respect to surface plane. The analysis area was approximately $150\text{ }\mu\text{m}$ in diameter by closing the apertures while the maximum analysis depth laid in the range of 4 – 8 nm. The surface elemental composition was calculated by the peak intensities of C (289.91eV), O (528.91eV), N (398.91eV) and S (164.91eV) on the survey spectra. Each sample was surveyed at three different locations and the average data were recorded.

Contact angles of the membranes were measured with the sessile drop method, using a goniometer (Contact Angle System OCA, DataPhysics Instruments GmbH). Membrane samples were dried in vacuum at room temperature for 24 h. DI water

droplets (about 2 μ l) were applied onto a flattened membrane surface and the profiles of the water drops were captured by an optical system to determine the contact angle using the instrument software. The reported data were averaged from 5 measurements at different locations on the membrane sample.

The surface charge properties of the membrane were determined by the streaming potential method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) with an electrolyte solution of 0.01 M potassium chloride (KCl) auto-titrated from pH 10 to 4. The streaming potential results were then calculated by its built-in software using Helmholtz-Smoluchowski equation to determine the membrane zeta-potential.

5.2.4. NF performance tests

The molecular weight cut-off (MWCO), i.e., the molecular weight of the solute with 90% rejection, of the NF membrane were measured on a bench scale cross-flow filtration unit at 1 bar using a 200 ppm solution of glucose, sucrose and glycerol, respectively. The rejection of the neutral organic solute was obtained from the concentrations of the feed and permeate solutions based on the total organic carbon measurements using a TOC analyzer (TOC-VCSH, Shimadzu, Japan).

The salt water permeability and salt rejection of the NF hollow fiber membrane and commercial flat sheet NF membranes (NF 270 and NF 90 from Dow chemical) were determined by the same cross-flow filtration unit under 2 bar pressure. A relatively high cross-flow velocity (0.5m/s) was maintained for the salt solution flow to minimize the concentration polarization effect. The salt solutions were always facing the membrane active layer where the inside-out filtration was performed for the hollow fibers. The single salt rejection tests (repeated for three hollow fiber membrane modules) were conducted using 1,000 ppm NaCl, MgCl₂, Na₂SO₄ and MgSO₄ solutions, respectively, based on the conductivity measurements (Ultrameter II, Myron L Company, Canada) of the permeate and feed water. For the simulated hard water tests, cation and sulfate concentrations in the

feed and permeate solutions were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer, USA).

5.3. Results and discussion

5.3.1. Characteristics of LBL hollow fibers

The characteristics of the PES membrane substrate and 4 types of NF hollow fibers, namely LBL*1.5 (deposited with PSS/PAH/PSS), LBL*2 (deposited with 2 pairs of PSS/PAH), LBL*1.5C and LBL*2C were studied and compared in this section including surface morphology, surface elemental composition, surface wettability, and the charge properties of the membranes. The characterization of the NF 90 and NF 270 membranes were not conducted in this study while some of their properties tabulated in Table 5-2 were from references (Nghiem et al. 2005; Song et al. 2011).

**Table 5-2. Properties of commercial NF membranes.
(Nghiem et al. 2005; Song et al. 2011)**

Membrane	Materials	Molecular weight cut-off (kDa)	Iso-electrical point	Pure water flux (l/m ² h bar)
NF 90	polyamide	0.1	4	6.7
NF 270	polyamide	0.2-0.4	3.5	13.1

The FE-SEM images of the hollow fiber membranes are presented in Fig.5-1. No visible change of cross-section morphology (Figs. 5-1(a) and (b)) was observed upon the LBL deposition and crosslinking due to the extremely thin polyelectrolyte multilayers at nanometer scales (Shiratori and Rubner 2000; Elzbieciak et al. 2009). However, it is clearly noticeable at the enlarged images of membrane inner surfaces that the surface pores on the substrate (Figs. 5-1(c)) were fully covered upon polyelectrolyte depositions (Figs. 5-1(d) and (e)). It is also not able to identify the

effect of the crosslinking on the LBL membranes and thus the other characterizations were performed thereafter.

Figure 5-1. FE-SEM images of hollow fiber membrane: (a) cross-section of LBL*1.5C; (b) enlarged cross-section of LBL*1.5C; (c) inner surface of PES substrate; (d) inner surface of LBL*2; (e) inner surface of LBL*1.5C

The X-ray photoelectron spectroscopy was used to examine the surface elemental composition of the membrane samples. Table 5-3 presents the average elemental compositions of all surveyed membranes while Fig. 5-2 illustrates the survey spectrums of the PES substrate and LBL*2 membrane as examples. As expected, the N peak at 398.91eV was absent from the PES substrate while distinctive N peaks were observed for all NF membranes, indicating that nitrogen element only originated from the deposited PAH polymers. On the other hand, although a considerable amount of sulfur present in the PES substrate, the minimum surface penetration (less than 10 nm) provided by the XPS analysis could ensure the S signal of a well-covered multilayer surface was only from the deposited PSS layer. In contrast, the O content not only came from the sulfonic groups of PSS but also from the trapped water molecules inside the polyelectrolyte matrices. Therefore it would not change with the S atom proportionally.

Figure 5-2. XPS spectra of hollow fiber membranes.

Table 5-3. XPS analysis of hollow fiber membranes.

	substrate	LBL*1.5	LBL*1.5C	LBL*2	LBL*2C
%C	72.4	67.1	67.1	69.1	69.8
%O	19.1	23	19.9	21.1	19.7
%S	8.5	4.8	6.8	3.2	4.9
%N	0	5.1	6.2	6.6	5.7
N/S ratio	0	1.1	0.9	2.1	1.16

Similar to pervious XPS studies on polyelectrolyte deposition (Chen and McCarthy 1997; Phuvanartnuruks and McCarthy 1998; Hyde et al. 2005), the amount of nitrogen and sulfur as well as the N/S ratio could be used to indicate the structure and composition of the multilayer surface. Based on the XPS results, the possible structure of the deposited layers and the effect of GA crosslink are sketched in Fig. 5-3. Due to the addition of high concentration NaCl into the polyelectrolyte solutions, relatively thick PSS and PAH layers were deposited on the substrate; and the distinct stratification of the layers were unlikely to be realized because of the inter-diffusion of the polyelectrolyte chains (Schlenoff and Dubas 2001). Hence, both amine groups from PAH and sulfo groups from PSS were found on the NF

membrane surface while their respective amount was mainly determined by the capping layer. For instance, the decrease of %S with the increase of %N were clearly observed when the capping layer switched from PSS (LBL*1.5 as in Fig. 5-3 (a).) to PAH (LBL*2 Fig. 5-3 (b).). Upon the introduction of glutaraldehyde molecules onto the membrane surface via the crosslinking, no significant increase of carbon content was detected. It might be due to the relatively small size of GA molecules, making them easier to penetrate inside the deposited layers to fill up the internal voids instead of forming another layer on the surface. Meanwhile, the O content were reduced after crosslinking which may due to the less membrane swelling with less water trapped inside the selective layers. Therefore, the membrane pore size was greatly reduced proved by the neutral solute rejection results which will be discussed in the later part. Also, it is possible that the GA crosslinking would cause the reorientation of the surface structure where free amine groups were immobilized onto the underlying structures by the GA moieties while more sulfonic groups were exposed to the surface, evidenced by the decreased surface N/S ratio for both crosslinked membranes shown in Figs. 5-3 (c) and (d).

Figure 5-3. Schematic drawings of NF hollow fibers.

As shown in previous studies (Chen and McCarthy 1997; Yoo et al. 1998; Malaisamy et al. 2011), the surface wettability /hydrophlicity of the polyelectrolyte multilayers is primarily controlled by the composition of outermost (capping) layer. In this study, the contact angle results of the hollow fiber membranes are shown in

Table 5-4. Since SO_3^- is more hydrophilic than NH_3^+ due to its higher tendency to form hydrogen bonding (Qi et al. 2012), the membrane surface wettability normally increase with a higher surface %S. Therefore, the LBL*1.5 membranes capped with a PSS layer were more hydrophilic than LBL*2 membranes capped with a PAH layer, which was also consistent with previous studies (Hsieh et al. 1997; Wong et al. 2004; Elzbieciak et al. 2008). Upon crosslinking, both membranes became more hydrophilic as more sulfonic groups appeared at the membrane surface. As a result, the observed membrane hydrophilicity was in the reverse order of the membrane surface N/S ratio mentioned earlier as $\text{LBL*1.5C} > \text{LBL*2C} \approx \text{LBL*1.5} > \text{LBL*2}$.

Table 5-4. Contact angle analysis of hollow fiber membranes.

substrate	LBL*1.5	LBL*1.5C	LBL*2	LBL*2C
$60.5^\circ \pm 2.5^\circ$	$56.8^\circ \pm 2^\circ$	$51.1^\circ \pm 1.5^\circ$	$78.3^\circ \pm 2.8^\circ$	$57.7^\circ \pm 1.2^\circ$

The zeta potential results of the substrate and NF membranes are presented in Fig. 5-4. Due to the steric hindrance and the swelling of polymer segment, the free charged groups from PSS (SO_3^-) and PAH (NH_3^+) existed not only on the outmost surface but also on the internal voids of the polyelectrolyte multilayers (as shown in Fig. 5-3). Instead of forming irreversible ionic bonds intrinsically, they are extrinsically compensated by the small counter-ions Cl^- or Na^+ from the supporting electrolyte during deposition (Schlenoff and Dubas 2001). The membrane surface charge was thus determined by their ratio and the protonation state of weak polyelectrolyte PAH upon the variation of pH value. As expected, the NF membranes showed typical ampholytic behaviors (Bohme et al. 2001). They were more negatively charged than the PES substate at the starting pH value of 10, as the degree of protonation for PAH was only about 15% at the moment (Ochiai et al. 1990), which was incapable to offset the negative charges of SO_3^- from PSS. However, at pH around 10, the LBL*2 and LBL*2C were more negatively charged than the LBL*1.5 and LBL*1.5C, respectively. It was beyond our expectation and

thus required further studies to investigate the possible reasons. The zeta potential readings were then gradually increased with increased degree of protonation of PAH upon titration towards the lower pH and eventually became positive across their respective iso-electrical points (IEP). Among the four NF membranes, the LBL*2 membrane possessed the highest IEP at around pH 8.5 with the upmost zeta potential curve followed by LBL*2C, LBL*1.5 and LBL*1.5C in the exact order of surface N/S ratio discussed earlier on. The newly formed $-C=N-$ on the crosslinked membrane was less basic than the original $-NH_2$ and thus carried weaker positive charge while protonated. This might be another reason for the less positively charged membrane after crosslinking.

Figure 5-4. Zeta potential of hollow fiber membranes.

5.3.2. Neutral solute rejection tests

The neutral solute rejection tests were conducted to estimate the MWCO of the NF membranes (Bowen and Mohammad 1998; Boussu et al. 2006). The properties of the three neutral solutes, glycerol, glucose and sucrose, are listed in Table 5-5 together with their rejections by the NF membranes. The membrane rejection

towards the glycerol was lower than expected probably due to its relatively linear structure compared with the spherical shaped glucose and sucrose. Nevertheless, it could be seen that the pore size of the membrane surface was reduced upon crosslinking with higher rejection against all tested neutral solutes. The MWCO of the LBL*2 and LBL*1.5C membranes were around 296 Da and 205 Da, respectively, by plotting their rejections against solute molecular weights. As for the LBL*2C membrane, due to the higher degree of crosslinking with more exposed amine groups, the selective layer was even tighter with a MWCO of 131 Da. However, it was not suitable for the low-pressure NF operation for the relatively low water permeability and thus was excluded from further study.

Table 5-5. Neutral solutes rejection performance*.

	LBL*2	LBL*1.5C	LBL*2C
Glycerol MW=92 Da $r_g=0.26$ nm	0	19.6% $\pm$ 2.1%	34.6% $\pm$ 1.8%
Glucose MW=180 Da $r_g=0.355$ nm	69.8% $\pm$ 1.2%	88.5% $\pm$ 1.1%	95.7% $\pm$ 0.5%
Sucrose MW=342 Da $r_g=0.471$ nm	98.1% $\pm$ 0.5%	98.4% $\pm$ 0.3%	99.1% $\pm$ 0.2%

*Tested at 1 bar using 200 ppm neutral solute solutions

5.3.3. Single inorganic salt rejection tests

The rejection mechanism of the LBL*2, LBL*1.5C and two commercial membranes were determined by performing the filtration test against four types of salt solutions with 1,000 ppm TDS (NaCl, Na₂SO₄, MgSO₄, MgCl₂) as suggested in various studies on NF membranes (Peeters et al. 1998; Schaep et al. 1998). It is clearly shown in Table 5-6 that the uncrosslinked LBL*2 membrane behaved like the “loose” NF 270 where the highest rejection against divalent co-ions (Mg²⁺ for

positively charged LBL*2 membrane and SO_4^{2-} for negatively charged NF 270 membrane) and the lowest rejection for divalent counter-ions (SO_4^{2-} for LBL*2 and Mg^{2+} for NF 270) were observed in accordance with Donnan theory. It suggests that the membrane rejection was mainly due to the charge effect in this case (Schaep et al. 1998). On the other hand, the crosslinked LBL*1.5C membranes showed a more than 95% rejection against each of Na_2SO_4 , MgCl_2 and MgSO_4 solutions respectively. Similar to the “tight” NF90 membrane, the size exclusion played a major role here. Therefore, it can be concluded that the significant difference on the Na_2SO_4 rejection between the LBL*1.5C and LBL*2 membranes (95% vs. 15%) was due to a different dominated rejection mechanism. Moreover, the LBL*1.5C membrane had only 33.5% of NaCl rejection (vs. 68.6% for NF90) and higher salt water flux in all tested salt solutions ($>10 \text{ l/m}^2 \text{ h bar}$ which was at least 60% higher in each case) as compared with NF 90.

Table 5-6. Separation performance of single salt solutions*.

	NaCl (%rejection)	SWP ($\text{l/m}^2 \text{ h bar}$)	MgCl_2 (%rejection)	SWP ($\text{l/m}^2 \text{ h bar}$)	Na_2SO_4 (%rejection)	SWP ($\text{l/m}^2 \text{ h bar}$)	MgSO_4 (%rejection)	SWP ($\text{l/m}^2 \text{ h bar}$)
LBL*2	58.6 ± 2.5	9.6 ± 0.5	98.1 ± 0.5	8.2 ± 0.2	15.0 ± 2.1	10.4 ± 0.2	93.0 ± 0.5	8.5 ± 0.6
LBL*1.5C	33.5 ± 3	14.4 ± 0.8	98.2 ± 0.6	10.6 ± 0.6	95.2 ± 0.6	12.7 ± 0.3	97.4 ± 0.3	13.8 ± 0.4
NF 270	37.1	12.5	42.9	11.2	98.1	10.1	96.3	10.5
NF 90	68.6	7.6	96.0	6.6	98.6	7.7	97.7	8.7

*Tested at 2 bar using 1000 ppm salt solution

5.3.4. Synthetic hard water rejection tests

It is known that the hardness removal efficiency of a membrane is affected by the total ionic strength and composition of feed solutions (Garcia-Aleman and Dickson

2004; Fang et al. 2014). Therefore, three synthetic hard waters with ionic strengths ranging from 3,000 to 10,000 ppm TDS were used shown in Table 5-7. The membrane performance against the tested feed water is presented in Table 5-8. As expected, the LBL*2 membrane rejection towards the Ca^{2+} and Mg^{2+} dropped significantly at an elevated SO_4^{2-} concentration (feeds #2 and #3). However, even for feed #3 with a TDS up to 10,000 ppm, the LBL*1.5C membrane could still maintain 90% hardness removal as compared with only 70% for the LBL*2 membrane. It was attributed to the tightened surface structure of the crosslinked membrane that was able to effectively reject SO_4^{2-} via size exclusion as discussed earlier on. As for the two commercial membranes, NF270 was not capable to treat all three feed water due to its negative charged nature and the relatively loose surface structure. In contrast, NF90 could effectively remove hard ions in feeds #1 and #2, relying on its tighter surface pores although it was also negatively charged. However, no permeate was collected after 30-minute filtration of feed #3 by NF90. This was probably due to the high osmotic pressure from the high rejection against Na^+ (over 50% for feeds #1 and #2 compared with only around 5% for LBL*1.5C). Thus, it was also not suitable for low-pressure NF operation impeded by the low permeability. In contrast, under the operating pressure of only 2 bar, the LBL*1.5C membrane could achieve a permeability of 6 $\text{l/m}^2 \text{ h bar}$ against feed #3. Its permeability was also at least three times higher than NF90 against the feeds #1 and #2 (12.5 $\text{l/m}^2 \text{ h bar}$ for feed #1 and 9.1 $\text{l/m}^2 \text{ h bar}$ for feed #2) with comparable hardness removal efficiencies of over 95%.

Table 5-7. Composition of mixed salt solutions.

	Feed #1	Feed #2	Feed #3
TDS (ppm)	3000	5000	10000
Total hardness (mg/l as CaCO ₃)	652	2306	2848
Mg ²⁺ (ppm)	103	257	293
Ca ²⁺ (ppm)	89	494	651
Na ⁺ (ppm)	905	838	1495
Cl ⁻ (ppm)	1757	2384	6557
SO ₄ ²⁻ (ppm)	146	1027	1004

Table 5-8. Separation performance of mixed salt solutions*.

Feed water	Membrane	Permeability (l/m ² h bar)	Hardness removal (%)	Ionic rejection (%)			
				Mg ²⁺	Ca ²⁺	Na ⁺	SO ₄ ²⁻
Feed #1 (3000 ppm TDS)	LBL*2	8.5	92.6	96.5	85	6	90.1
	LBL*1.5C	12.5	98	99	96	5.7	94.5
	NF 270	9.9	60.8	68.2	46.6	25.8	98.6
	NF 90	3.5	98	98	97.6	53.7	98.4
Feed #2 (5000 ppm TDS)	LBL*2	8.2	80	91.1	70.1	-6.8	76.9
	LBL*1.5C	9.1	95	98.4	91.8	7.3	86
	NF 270	6.8	74.4	81.7	68.1	28.4	98.7
	NF 90	2.3	98.4	97.9	98.8	49.4	98.7
Feed #3 (10000 ppm TDS)	LBL*2	5.8	70.7	86.8	58.6	-5.2	48.2
	LBL*1.5C	6	90.3	96.2	85.8	0	80.2
	NF 270	5.1	74.6	84	67.6	36.8	98.7
	NF 90	-	-	-	-	-	-

*Tested at 2 bar

5.4. Conclusions

The glutaraldehyde (GA) crosslinking was applied on the selective layer of NF hollow fiber membranes made by layer-by-layer (LBL) polyelectrolyte assembly to enhance the water softening performance of feed water in the presence of divalent counter-ion, SO_4^{2-} . The characteristics of the crosslinked NF membranes were studied thoroughly and their NF performances were compared with uncrosslinked LBL membranes and two commercial membranes NF90 and NF270.

The possible structure of the deposited layers and the effect of GA crosslinks was proposed based on the membrane characterization results. It was found that the crosslinking could tighten the membrane surface pores with increased hydrophilicity while the membrane surface charge was reduced. Therefore, mainly based on the size exclusion, the crosslinked LBL*1.5C membrane showed more than $10 \text{ l/m}^2 \text{ h bar}$ permeability with above 95% rejection to each of 1,000 ppm MgCl_2 , MgSO_4 and Na_2SO_4 solution under 2 bar pressure. It was also proven to be more suitable for the low-pressure water softening application at 2 bar in all tested feed water with the presence of SO_4^{2-} and TDS up to 10,000 ppm in terms of both permeability and hardness removal efficiency when compared with commercial NF 270 and NF 90 membranes.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The layer-by-layer (LBL) polyelectrolyte deposition technique has been successfully applied on a PES hollow fiber substrate to make novel LBL hollow fibers for forward osmosis (FO) with low draw solution concentration and low-pressure (2 bar) water softening application for the first time. A three-stage membrane fabrication scheme was adopted in the order of outer surface static deposition, semi-dynamic inner surface deposition and glutaraldehyde crosslinking post-treatment. The important findings and conclusions are summarized as follows:

- The LBL polyelectrolyte deposition technique can be applied on both outer (od-LBL) and inner surfaces (id-LBL) of a PES hollow fiber substrate to form NF membranes.
- The od-LBL hollow fibers exhibited superior FO performance compared with literature data. However, for the hollow fiber substrate, the inner surface is more suitable for LBL deposition which is probably due to the formation of a more effective selective layer with higher surface charge density and smaller pore sizes produced by the inner deposition.
- In NF tests, the id-LBL membranes could not only withstand higher operating pressure but also possess superior hardness rejection especially in high concentration mixed salt solutions (more than 95% rejection to Mg^{2+} and Ca^{2+} in a 5000 ppm total dissolved salt (TDS) mixture under 4.8 bar).
- As for the FO process, with only two layer deposition, the id-LBL membranes also demonstrated significant performance improvement with increased water flux (up to $70 \text{ l/m}^2 \text{ h}$ using 0.5 M MgCl_2 as draw solution in active layer facing draw solution configuration) and reduced salt leakage (around $0.5 \text{ g/m}^2 \text{ h}$ using 1 M MgCl_2 draw solution in active layer facing feed water configuration).

- The LBL membrane possessed superior chemical and mechanical stability with great potential in future practical applications.
- It is found later that the id-LBL membrane rejection was drastically deteriorated in the presence of SO_4^{2-} in the feed water due to the weakened charge effect while the size *exclusion was expected to play a more important role in the real situation. Thus the GA crosslink was adopted to enhance its water softening performance* of synthesized hard water in the presence of divalent counter ion SO_4^{2-} .
- The challenges for the low-pressure water softening membrane include (a) the presence of SO_4^{2-} in the feed water, which tends to deteriorate positively charged NF membrane retention to divalent ions; (b) high salinity feed water up to 10,000 ppm TDS; (c) 2 bar operating pressure that requires the membrane to have a good $\text{Mg}^{2+}/\text{Na}^+$ selectivity and less mass transfer resistance in the substrate; and (d) better separation performance as compared with the state-of-the-art and commercial NF membranes.
- The possible structure of the deposited layers and the effect of GA crosslink were proposed based on the membrane characterization results. It was found that the crosslinking could tighten the membrane surface pores with increased hydrophilicity while the membrane surface charge was reduced.
- Mainly based on the size exclusion, the crosslinked LBL*1.5C membrane showed more than $10 \text{ l/m}^2 \text{ h bar}$ permeability with above 95% rejection to each of 1,000 ppm MgCl_2 , MgSO_4 and Na_2SO_4 solutions under 2 bar pressure. It was also proven to be more suitable for the low-pressure water softening application at 2 bar in all tested feed water containing SO_4^{2-} and TDS up to 10,000 ppm in terms of both permeability and hardness removal efficiency when compared with commercial NF 270 and NF 90 membranes.

6.2. Recommendations

The future plans of this project are proposed in three directions: (1) to scale up the crosslinked LBL membrane with the best water softening performance for pilot study and possible commercialization; and (2) to explore the further applications of LBL hollow fibers by modifying membrane properties such as surface pore size and charge density based on the current PES substrates; (3) to develop microfiltration (MF) hollow fiber substrates suitable for LBL deposition in collaboration with other colleagues and explore the possible applications. All approaches will be briefly introduced here with some preliminary results.

The scale-up process involves two major tasks: the fabrication of large scale membrane modules and the followed LBL deposition on those modules. Currently, two types of 2-inch (in diameter) modules with an effective length of 25 cm and 60 cm, respectively, were successfully fabricated by slow epoxy resin potting in either static or centrifuged process as shown in Figure 6-1. The effective membrane area was 0.15 m^2 and 0.36 m^2 respectively with a packing density of $324 \text{ m}^2/\text{m}^3$ which is expected to be tripled with the development of appropriate LBL deposition scheme at latter stages. On the other hand, the current syringe aided semi-dynamic deposition method became ineffective to handle the increased amount of chemicals. Therefore, alternative deposition methods such as the pumping or sucking through a peristaltic pump or the combined use of syringe and pump are to be evaluated. Meanwhile, various deposition conditions will also be modified to optimize the module performance.

Figure 6-1. Pilot scale membrane modules.

Besides the FO and water softening process, the LBL deposited membranes can be used for other applications due to the highly controllable polyelectrolyte multilayer properties, in particular, the surface charge and the surface pore structure. By careful selection of polyelectrolyte pairs and modification of deposition condition, it is possible to tailor the separation properties of LBL membranes for targeted use. For example, highly permeable membranes with high surface charge and loose pore structure are suitable for heavy metal removal for their relatively high valences and large hydrated radius. Also, it is able to precisely control the molecular weight cut-off (MWCO) of the membranes to separate some specific organic matters such as dyes and proteins based on electrostatic and/or repulsion size exclusion. Currently, the development of LBL NF membranes is undergoing for reverse osmosis pre-treatment and the stepwise separation of pharmaceutical organics.

Last but not least, as introduced in the literature review, the layer-by-layer assembly is not only feasible on the membrane surface but also can be performed inside the porous structure, especially for the MF membranes to utilize higher surface areas for some specific applications. The thermally induced phase separation (TIPS) process is one of well studied techniques to prepare MF membranes. It offers several notable advantages such as very low tendency for defect formation and effective control of the final pore size (Su et al. 2007). During the membrane preparation, a polymer is firstly dissolved in a diluent at an elevated temperature. The homogenous polymer solution is then cooled down to induce phase separation. Finally, after the polymer is solidified by either crystallization or glass transition, the diluent is removed by extraction or drying, leading to the formation of a porous membrane. A number of polymers such as polypropylene, polystyrene, polyethylene and cellulose acetate have been used for membrane fabrication via TIPS process. Among them, poly(vinylidene fluoride) (PVDF) has drawn great attention in recent years for its semi-crystalline, thermal stability and chemical resistance and therefore is chosen as the primary material for future experiments. Different spinning conditions such as the dope composition and spinning temperature will be investigated extensively to optimize the membrane structure and its intrinsic performance. Afterwards, with any necessary post-modification

such as in situ polymerization and hydroxylation, the LBL assembly will be performed inside membrane pore structures via dynamic deposition.

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