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Application of Multilayer Thin Film Technology in Desalination Membrane

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<http://dx.doi.org/10.5772/intechopen.68375>

Abstract

Membrane-based desalination is the fastest growing technology in the area of desalination. Reverse osmosis (RO) and nanofiltration (NF) have been established in the last couple of decades; meanwhile, forward osmosis (FO) has begun to find its own place in the field of desalination. Typical commercial polyamide (PA) thin film composite (TFC) membrane has been mostly used in those membrane processes, but it has no drawback. Recently, a versatile, robust technique in preparing ultra-thin films, so-called layer-by-layer assembly (LbL), was adopted in fabrication of desalination membrane. This chapter highlights the most important literatures in the application of LbL assembly for preparing RO, NF and FO membranes, the obstacles and future works, which are essential for those who wish to work in the field.

Keywords: layer-by-layer, dip-LbL, spray-LbL, spin-LbL, reverse osmosis, nanofiltration, forward osmosis, surface modification

1. Introduction

United Nations Environment Programme reported that two out of every three people will live in water-stressed areas by the year 2025. In 2008, 450 million people in 29 countries suffered from water shortages [1]. In addition to that, many more people have been suffering from consuming contaminated water that may cost human lives [2]. These problems just come from domestic uses, which account for 5% of the total water consumption. Meanwhile, 75% of total global water consumption comes from agricultural uses and balance for industrial uses. So far, ground water represents about 90% of the world's readily available freshwater

resources, and 1.5 billion people depend on it for their drinking water. Freshwater resources are so unevenly distributed that makes most people lack access to freshwater supply [1].

Desalination has been considered as the only method that can provide freshwater for drinking from traditional sources such as ground water, sea water and other saline aquifers [3]. These traditional sources of water account for 97.5% of all water on the Earth. Thus, capturing even a tiny portion of that water will have a significant impact on reducing water scarcity [3]. As generally known, the main desalination technology can be divided into two main categories, that is thermal-based and membrane-based desalination technology. Membrane technology, particularly RO, has been a dominant technology in the field of desalination membrane. Due to significant improvement of RO process in the last four decades, it has been projected to be the leading desalination technology in general and is mostly used in almost all areas except in the countries having readily available fossil fuels [4].

Since Cadotte developed thin film composite (TFC) membrane polyamide (PA) RO membrane using interfacial polymerization in 1980 [5], it has been mostly used in desalination membrane. However, commercial TFC RO still faces a major problem, particularly bio-fouling. This is a result of hydrophobic and rough nature of the PA membrane itself and also partly due to the fabrication technique. The method is quite powerful to prepare thin films but lacks fine control over surface properties.

In the middle of the 1990s, a rediscovery of the so-called layer-by-layer method has opened a new paradigm in the preparation of an ultra-thin layer. LbL assembly offers nano-level control over several surface properties such as thickness, surface composition, surface roughness and so on. Not to mention, the flexibility in terms of material opened the room for improvement in terms of chemistry of the membrane, a field that has long been considered mature [6].

Therefore, the purpose of this chapter is to review recent activities in the field of LbL assembly, particularly those used in preparing the membrane for desalination. At the beginning, we will briefly highlight some important aspects about LbL assembly in general. We will then focus on method of preparation, some important results, drawbacks and future challenges related to the application of LbL in desalination membrane. In addition to that, we will also highlight some recent works related to the application of this method in the modification of commercially available membranes used in the field of desalination. We limit our discussion to the application of this membrane in separating or removing ions of salt only because there have been many reported works as well in the application of LbL NF, for instance, for removing organic contaminants from water, etc.

2. Layer-by-layer

2.1. Dip-LbL (d-LbL)

The root of LbL assembly might be traced back to 1966 when Iler introduced a novel technique in which colloidal oppositely charged particles can be assembled into layer-by-layer films [7]. However, it was only after Decher reintroduced a similar technique for polyelectrolytes multilayer (PEM) assembly that the technique became very popular

in colloidal and interfacial science [8]. After various testing and proofing, particularly for different multilayer precursors [9–13], the systematic way was then reported in 1997 and became the most-cited article in the field of chemistry for 10 years (1998–2008) [14]. The classic approach to assemble PEM thin films is by alternately dipping the substrate into two oppositely charged polyelectrolytes as can be seen in **Figure 1**.

Although LbL assembly was initially invented by making use of electrostatic interaction between the two oppositely charge polyelectrolytes or colloidal particles, nowadays, it can also be formed via donor/acceptor [15, 16], hydrogen bonding [17, 18], covalent bonds [19–21] and stereo-complex formation [22, 23]. The precise structure of each layer depends on a set of control parameters such as polyelectrolyte concentration, adsorption times, ionic strength [24], pH [25] or temperature [26].

2.2. Spray-LbL (Sr-LbL)

Sr-LbL was introduced by Schlenoff [27] by employing poly(diallyl dimethyl ammonium chloride) (PDADMAC) and poly(styrene sulfonate) (PSS) on silicon wafer. Using this technique, similar film structures and properties to d-LbL film can be achieved in shorter deposition time. It was reported that a fully automatic system of this technique can fabricate the film of the same quality as a d-LbL film 25 times faster [28–30]. The main drawbacks of Sr-LbL are still relatively slow polyelectrolyte assembly coupled with inefficient use of polymer solution, which is about 99% of the polymer solution that is rinsed off during film preparation. However, if the size of the substrate is the concern, then, this technique is more suitable than d-LbL [27]. Sr-LbL can also be used to conformally coat individual fibres within a textured surface of hydrophobic textile [29].

2.3. Spin LbL (SA-LbL)

SA-LbL was introduced by Hong *et al.* in 2001 [31, 32] and Chiarelli *et al.* in the same year [33]. Hong *et al.* successfully fabricated very smooth thin layers with controllable thickness that comprised of the combination of nanoparticles and polyelectrolyte. The major difference

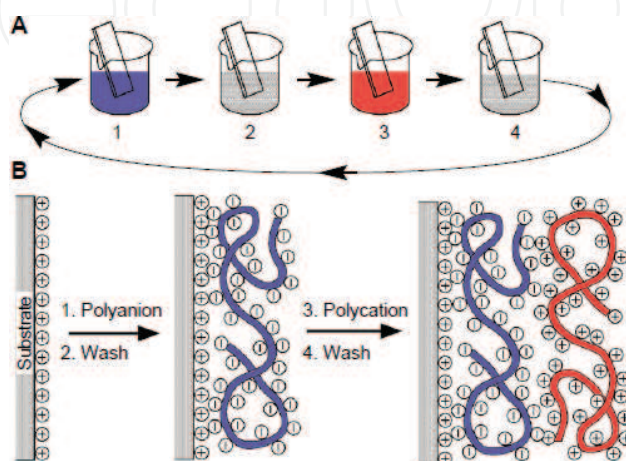


Figure 1. A schematic diagram of dip-layer-by-layer assembly (adapted from Ref. [14]).

between d-LbL and SA-LbL is the way polyelectrolytes are deposited on the substrate. As it is generally known, in the case of d-LbL, the substrate is immersed in polyelectrolyte solutions, while in the case of SA-LbL, only a small amount of polyelectrolyte is injected onto the spinning substrate.

It was reported that the SA-LbL film is several times thicker than d-LbL film for the same number of bilayers, which is due to different adsorption mechanisms. In d-LbL, the polymer chain will be adsorbed on the substrate under influence of electrostatic force and then followed by chain rearrangement. Meanwhile, in SA-LbL, due to high-speed spinning, the adsorption, the rearrangement of polyelectrolyte chains and water removal occur simultaneously. Quick water removal increases polyelectrolyte concentration in a very short time and also removes screening effect by water molecules. This in turn promotes faster adsorption and stronger electrostatic force; hence, more polymer chains are adsorbed within short time and result in a thicker film than d-LbL film [31].

Air shear force that occurs due to the relative movement between spinning substrate and air enhances the planarization of multilayer film, significantly reduces the surface roughness of the film and enhances mechanical integrity [34]. The above features are indirect evidences that SA-LbL film has a highly ordered internal structure [31], and experimentally, it has been revealed by neutron reflectivity study. Because a highly ordered internal structure can be obtained in much shorter time than conventional d-LbL or Sr-LbL, SA-LbL is considered to be more “technologically friendly” [34].

3. Layer-by-layer application

3.1. LbL for separation membrane

3.1.1. Nanofiltration

Due to its charged characteristic, polyelectrolyte LbL membrane has been found to be promising for NF application. There have been many works done and are ongoing in this area. Some representative works are listed in **Table 1**. We selected the best performance in terms of flux and selectivity of $\text{Cl}^-/\text{SO}_4^{2-}$ from each work so they can be compared to each other. All those reported works used d-LbL approach unless it is stated differently.

The earliest notable work in d-LbL NF membrane perhaps was done by Krasemann and Tieke in 1999 [35]. They suggested the mechanism of salt rejection by LbL membrane similar to that of bipolar membrane as can be seen in **Figure 2**. However, some fundamental studies showed that PEM films do not exhibit an internal structure as originally projected and commonly depicted. There is significant intertwine between polyelectrolytes as a consequence of charge compensation. In d-LbL assembly, this charge compensation is most likely attained since the contact time between adjacent layers is sufficient to achieve it [36]. In accordance with this statement, our work using SA-LbL assembly also showed no significant increase in rejection

LbL film substrate	Main result	Testing condition	Ref
(PAH/PSS)-PAN/PET with 20–200 nm pore size ¹	(PAH/PSS) ₆₀ showed selectivity of Na ⁺ /Mg ²⁺ = 15.1; Cl ⁻ /SO ₄ ²⁻ = 9.9	0.1 M for each of NaCl, MgCl ₂ and NaSO ₄ , membrane active area: 4.53 cm ² , dead end cell	[35]
(PAH/PSS)-porous alumina with 20 nm pore size	(PAH/PSS) ₅ showed selectivity of Cl ⁻ /SO ₄ ²⁻ = 7	0.1 M for each of KCl and K ₂ SO ₄ , membrane active area: 2 cm ² , dead end cell	[38]
(PAH/PSS)-porous alumina with 20 nm pore size	(PAH/PSS) _{4.5} showed individual rejection of MgSO ₄ = 96%, NaCl = 29% and selectivity Cl ⁻ /SO ₄ ²⁻ = 30	1000 ppm for each of NaCl, MgSO ₄ ; P = 4.8 bars; membrane active area: 1.5 cm ² ; cross flow cell.	[39]
(PSS/PDADMAC)-porous alumina	(PSS/PDADMAC) _{4.5} showed WF = 2.4 m ³ /m ² .day; rejection of SO ₄ ²⁻ = 92.3; selectivity Cl ⁻ /SO ₄ ²⁻ = 15	1000 of Cl ⁻ , 1000 ppm of SO ₄ ²⁻ ; P = 4.8 bars; membrane active area: 1.5 cm ² ; cross flow cell.	[42]
(PAH/PSS) ₅ (PAH/PAA) _{2.5}	Selectivity of Cl ⁻ /SO ₄ ²⁻ = 150	0.1 F for each of KCl and K ₂ SO ₄	[47]
Support: Porous alumina with 20 nm pore size	Selectivity of Cl ⁻ /SO ₄ ²⁻ = 360	Membrane active area: 2 cm ² .	
After heat-induced crosslinking at 115°C			
(PDADMAC/PSS)-PES UF 50 kDa MWCO ²	(PSS/PDADMAC) _{4.5} showed WF = 1.6 m ³ /m ² .day; rejection of SO ₄ ²⁻ = 96%; selectivity Cl ⁻ /SO ₄ ²⁻ = 32	1000 of Cl ⁻ , 1000 ppm of SO ₄ ²⁻ ; P = 4.8 bars; membrane active area: 1.5 cm ² ; cross flow cell.	[48]
(PAH/PSS)/(PAH/PSSMA)-PAN UF ³	(PAH/PSS) ₁ /(PAH/PSSMA) ₁ showed WF = 28.6 L/m ² .h, rejection of Na ₂ SO ₄ = 91.4%	1000 ppm Na ₂ SO ₄ , P = 2 bars membrane active area: 23.75 cm ²	[40]

¹ PAN/PET = polyacrylonitrile/polyether terephthalate.

² PES = polyethersulfone.

³ PSSMA = poly (4-styrenesulfonic acid-co-maleic acid).

Table 1. Selected work for NF prepared from polyelectrolyte multilayer membrane using LbL assembly.

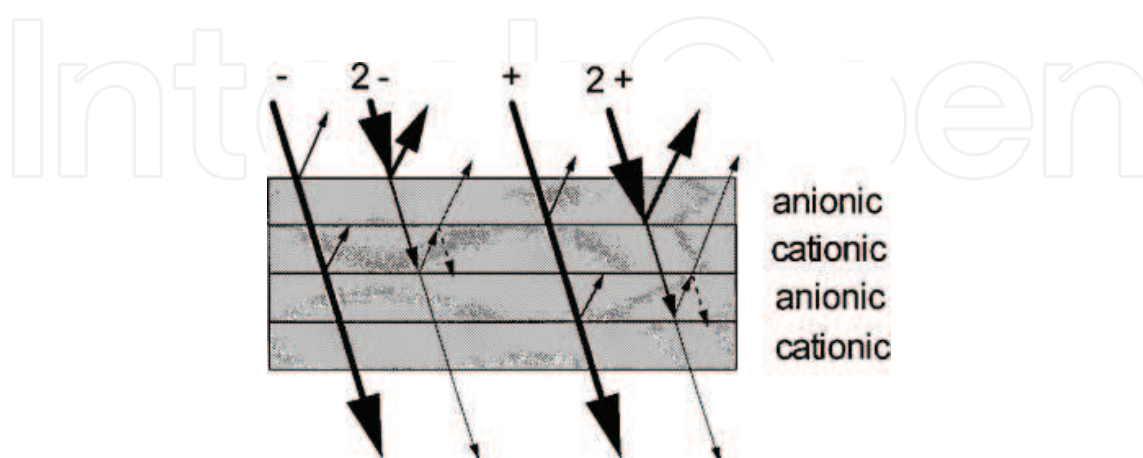


Figure 2. A rejection model of multi-bipolar membrane (adapted from Ref. [35]).

by doubling the number of layers, even though it is well known that the contact between layers is very short in this type of LbL assembly. This is evidence that even in short time, charge compensation is attained to some extent. It is also evidence that a bipolar mechanism may not be suitable, and this type of membrane rather follows a typical mechanism for NF or RO membrane [37]. It was also investigated that by changing the outermost layer, the anion flux changes significantly suggest that only uncompensated charges lie near the film/solution interface that have significant effect in ion rejection [38, 39].

It is widely known that ion rejection is one of the most importance performance indicators of a membrane. Aside employing highly charged polyelectrolytes which can improve rejection from the outermost layer, using dynamic LbL assembly seems quite helpful in this aspect. In this type of LbL assembly, polyelectrolyte solution is forced to pass the support layer and leaves behind the polyelectrolyte on the surface of the support layer. Dynamic LbL produces a more compact and tighter LbL membrane, which in turn increases the rejection [40]. There is also so-called semi-dynamic LbL assembly, which involves the dynamic introduction/replacement of solution into the fibre lumen by syringes followed by static contact for desired time. This technique is quite useful for hollow fibre membrane as the support [41].

In addition to ion rejection, flux is also considered as the most important performance indicator. Many membranes have high flux due to swelling which in turn will reduce the rejection. From investigation of several frequently used PEM pairs, it was reported that solution fluxes decrease in the following order: PDADMAC/PSS > Poly(allylamine hydrochloride) PAH/PSS > PDADMAC/Poly(acrylic acid) PAA >> PAH/PAA [42]. PDADMAC/PSS, for instance, permits higher flux than PAH/PSS due to higher degree of swelling [43]. In addition to swelling, highly porous support can also contribute to higher flux because it helps in reducing membrane resistance. Several methods have been used to produce highly porous support such as using electrospun nanofiber [44] or incorporating nanoparticles such as montmorillonite (MMT) or silica gel (SG). For example, polyvinyl alcohol (PVA) mixed with 1 wt% montmorillonite (MMT) can achieve porosity of 80% [45]. Likewise, PAN support mixed with 1 wt% SG can also achieve porosity of 80% [46].

3.1.2. Forward osmosis

The application of LbL assembly for NF is quite promising as can be seen in the previous section. There have been many works done and are ongoing in that area; meanwhile, the use of LbL assembly for fabricating FO is still at its infancy. The main results from FO mode of testing of several LbL FO membranes can be seen in **Table 2**. It is important to note that the information given in **Table 2** is only part of the works that showed the best performance in terms of water flux (WF) and salt to water flux ratio (SWFR) with active layer facing draw solution (ALDS) testing mode. It is known that ALDS mode shows higher initial water flux compared to ALFS mode, but it is also prone to internal fouling because foulants enter the porous support easily. This type of fouling in fact is much more difficult to be cleaned. In order to overcome this problem, a double-skinned design was proposed [49]. Double-skinned layer approach uses active layer deposited on both surfaces with the support layer, which will be in between as can be seen in **Figure 3**. Hence, it will prevent the foulants from entering the membrane from the support layer side.

As previously discussed, swelling of the membrane can result in higher flux due to expansion of the pores. For NF application, in which the membrane is exposed to relatively low salt concentration solution, swelling may not cause serious problems, but in the case of FO or RO, swelling degree can be very high and significantly decreases the salt rejection. Several attempts have been done to enhance LbL film stability, for example, by using crosslinking. Glutaraldehyde (GA) is the mostly used chemical crosslinker as can be seen in **Table 2**. With this crosslinking, LbL membrane can maintain its structure and performance and showed quite comparable performance with the commercial membrane [50]. Besides GA, UV light can also be employed to further increase the extent of crosslinking [51]. The mechanism of GA and UV light crosslinking can be seen in **Figure 4**. Some polyelectrolytes that contain carbonyl and amine functional group can be crosslinked simply by heating at 180°C, and this results in a polyamide-like layer which has better stability and lower swelling degree [52].

So far, the preparation of LbL membrane is mainly from polyelectrolytes. Recently, the researcher has started utilizing the technique for fabrication of LbL membrane using methylphenylene diamine (MPD) and trimesoyl chloride (TMC), two most commonly used

LbL film substrate	LbL assembly	Result/testing condition ⁴	Ref.
(PAH/PSS)-PAN	Dip, crosslinked using GA	(PAH/PSS) ₃ showed WF of 105.4 L/m ² .h and SWFR of 2.8 mM	[50]
	Dip, crosslinked using GA, double-skinned layer	(PAH/PSS) _{3,3} showed WF of 35.5 L/m ² .h and SWFR of 4.86 mM	[49]
	Dip, crosslinked using GA, embedded silver nanoparticle	(PAH/PSS) _{2,5} showed WF = 42 L/m ² .h and SWFR = 0.84 mM / FS: 10 mM NaCl	[55]
	Dip, crosslinked using combined GA and UV light	(PAH/PSS) ₃ with UV exposure = 2 h showed WF = 15 L/m ² .h and SWFR = 0.8 mM	[51]
(PAH/PSS)-hollow fibre PES	Dip	(PAH/PSS) ₆ showed WF = 40.5 L/m ² .h and SWFR = 2.1 mM	[56]
	Semi-dynamic	(PAH/PSS) ₂ inner deposited layers showed WF = 73.5 L/m ² .h and SWFR = 0.6 mM	[41]
(PAH/PAA-PSS)-PEI	Dip, crosslinked using GA	(PAH/PAA-PSS) ₃ showed water flux of 28 L/m ² .h and SWFR of 0.74 mM/dead end cell	[57]
(CHI/PAA)-(PVA+MMT-TA+ LiCl)	Dip	(CHI/PAA) ₃ with MMT = 1 wt% showed WF = 19 L/m ² .h and SWFR of 0.09 mM/DS: 0.5 M NaCl, dead end cell	[45]
(PAH/PSS)-(PAN+SG)	Dip	(PAH/PSS) ₃ with SG = 1 wt% showed WF = 77.9 L/m ² .h and SWFR = 0.94 mM	[46]
(MPD/TMC)-(PEI/PAA coated PAN)	Dip	10 layers of molecular LbL showed WF of 33 L/m ² .h and SWFR of 1.7 mM/DS: 0.5 M NaCl	[53]

⁴All reported default testing condition is DS = 0.5 M MgCl₂, FS = pure water, cross flow system, unless it is mentioned differently. π_{NaCl} at 0.5 M = 22.74 atm and π_{MgCl_2} at 0.5 M = 32.65 atm.

Table 2. The work progress for FO prepared from polyelectrolyte multilayer membrane using LbL assembly.

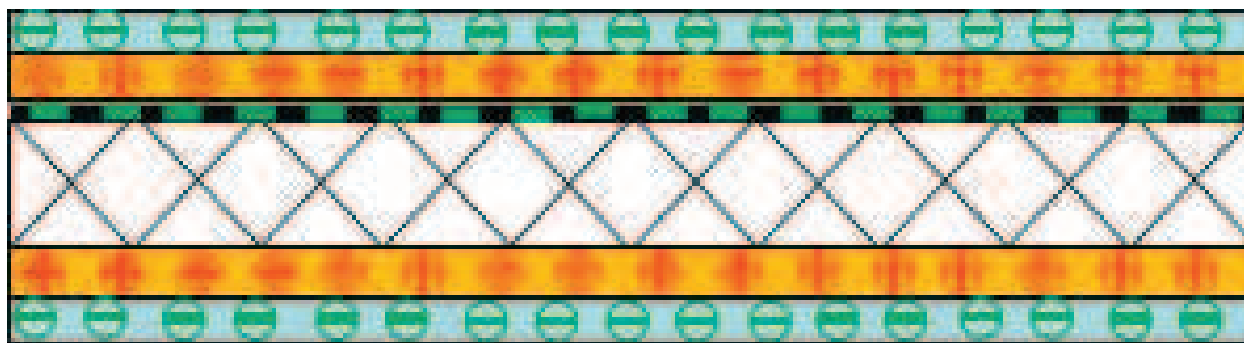


Figure 3. A conceptual illustration of doubled-skin LbL membrane (adapted from Ref. [49]).

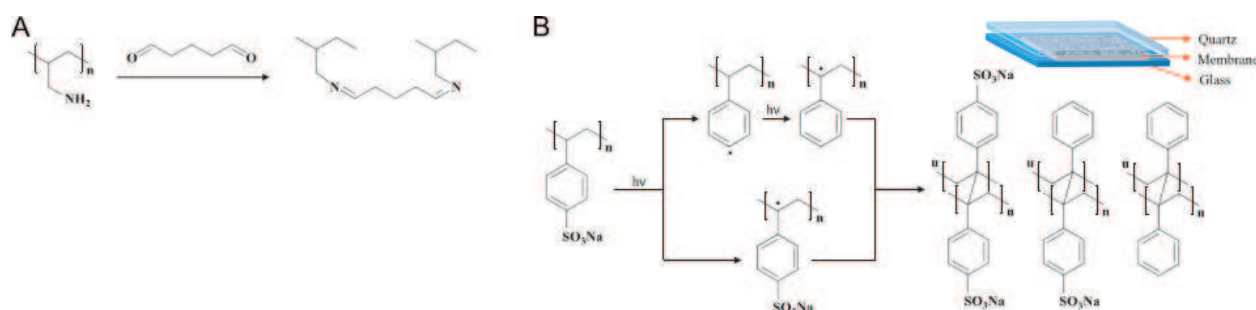


Figure 4. A schematic mechanism of crosslinking (A) using GA linker and (B) using UV light (adapted from Ref. [51]).

monomers for PA. This method is known as molecular layer-by-layer assembly (m-LbL) [53]. The mechanism of m-LbL is shown in **Figure 5**. Compared to several typical LbL FO and commercial FO membranes, m-LbL FO membrane showed superior performance for both ALDS and ALFS modes. Having said that, m-LbL FO membrane still has problems with stability and irreversible defect, especially after exposing it to very high salt concentration solution, for example, at 2 M NaCl. This instability is most likely due to relatively weak interaction between m-LbL film and the support. One of the approaches to enhance this interaction is by employing interlayers that will be discussed in more detail in the RO section.

3.1.3. Reverse osmosis

The use of LbL assembly for fabricating RO membrane is one of the most challenging applications because a typical RO membrane is tested at relatively high salt concentration up to 32,000 ppm with high operating pressure. Many polyelectrolyte multilayer films are not stable when exposed to such conditions.

The earliest work in this field to the author's knowledge was done by Jin *et al.* in 2003 [58]. Polyvinyl Amine (PVAm)/Polyvinyl sulphate (PVS) was used in their work and deposited on PAN/PET support using d-LbL assembly. Membrane performance was examined at a pressure of 40 bars, with NaCl concentration of 584.4 ppm using dead end cells with membrane active area of 36.8 cm². The result showed salt rejection of 93.5% and permeability of around 0.11 L/m².h.bar. Similar work using thermally induced PAH/PAA deposited onto

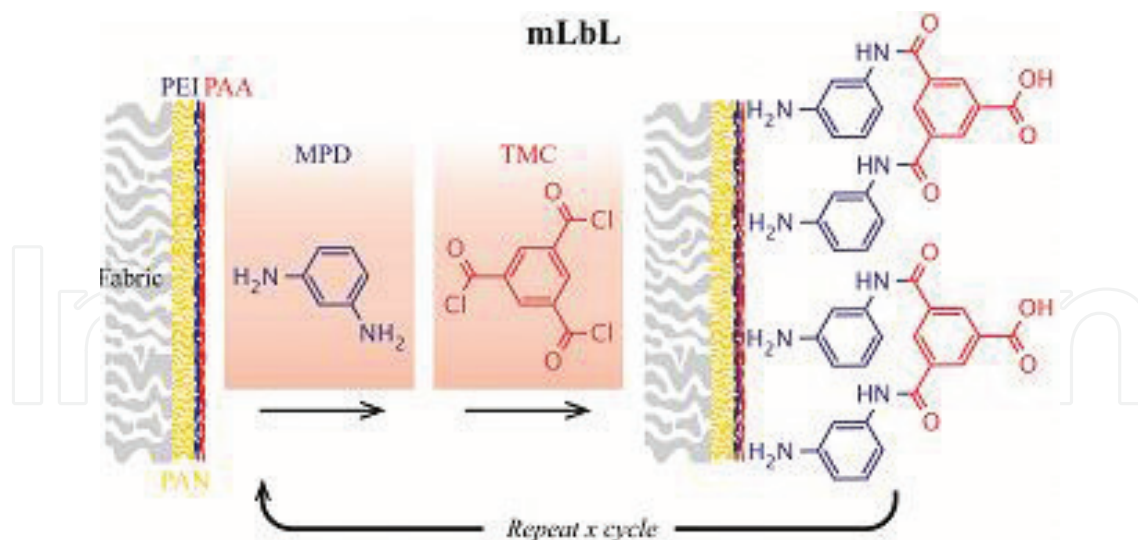


Figure 5. A schematic diagram for m-LbL process (adapted from Ref. [54]).

PSF supports showed salt rejection of around 81% with water permeability of 0.35 L/m².h.bar tested at a pressure of 20 bars and NaCl concentration of 2000 ppm using cross flow cells with active area of 13.85 cm² [59].

From the above literature review, almost all RO and FO LbL membranes were tested at low salt concentrations. Meanwhile, RO and FO membranes are normally used to treat water with rather high salt concentrations. There has been an issue with LbL film stability when it is exposed to such solution. Some PEMs are quite stable even without crosslinking. For instance, it was reported that 35 layers of PAH/PAA were successfully deposited on PSF support using SA-LbL and tested at pressure of 48.6 bars and NaCl concentration of 15,000 ppm using cross flow cells with active area of 42 cm². The test showed very stable performance with salt rejection of around 88% and water permeability of 0.22 L/m².h.bar. This work was considered the first attempt to apply SA-LbL for fabricating RO membrane [60]. Besides that, the use of Sr-LbL to fabricate RO membrane was also investigated, for example, assembly of clay (laponite (LAP)) and polyelectrolyte multilayers on the top of PSF support. (PAH/PAA) (PAH/LAP) deposited at pH 5 and tested at pressure of 18 bars, with NaCl concentration of 10,000 ppm using dead end permeation cells showed salt rejection of 89% with water permeability of 2.82×10^{-13} m²/Pa.s. [61].

As previously mentioned, the use of m-LbL for RO membrane was also studied (see **Figure 5**). Using m-LbL, the membrane performance can be finely tuned by simply varying the number of layers. In general, as the number of layers increases, the flux decreases and rejection increases as can be seen in **Figure 6**. For instance, with 10 layers of m-LbL only, salt rejection of around 96% coupled with flux of 82% higher than IP TFC PA membrane was attained. In addition to this remarkable result, the surface roughness of this m-LbL membrane was only 3.4 nm, which was much smoother than surface roughness of IP PA TFC (i.e. 45.1 nm in this study) [54].

Recently, the same group of researchers investigated the role of interaction between m-LbL as active layer and the support layer, that is, PAN by showing the performance difference between hydrolyzed PAN (HPAN) and non-hydrolyzed PAN (see **Figure 7**) [62].

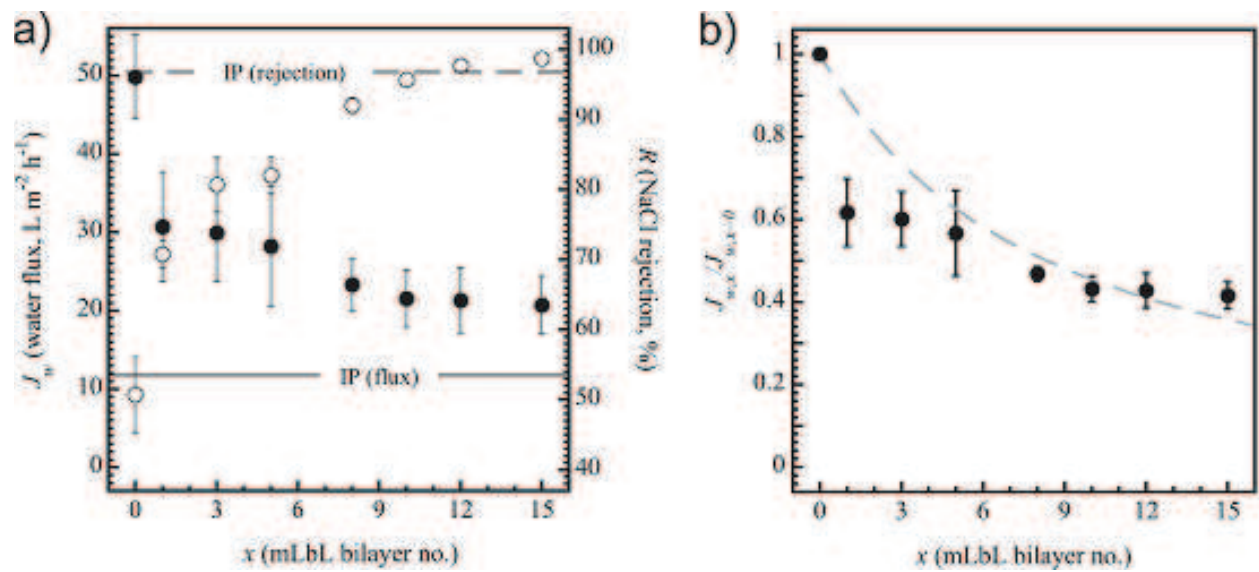


Figure 6. (a) Water flux (J_w , filled symbols) and NaCl rejection (unfilled symbols) as functions of a number of layers. (b) Normalized flux as a function of a number of bilayers (membrane was tested at NaCl concentration of 2000 ppm and pressure of 15.5 bars; adapted from Ref. [54]).

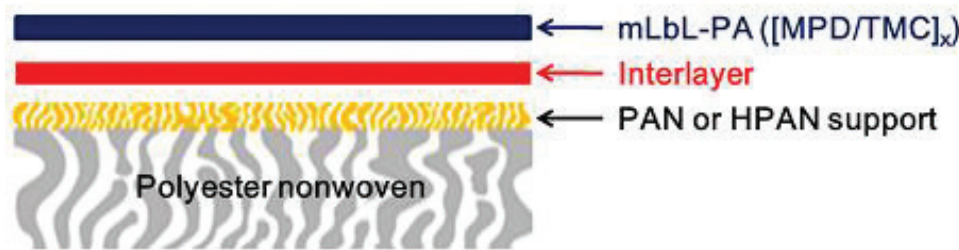


Figure 7. A conceptual design of m-LbL TFC PA membrane with interlayer (adapted from Ref. [62]).

As can be seen in **Figure 8**, deposition of m-LbL PA on the top of HPAN resulted in much higher rejection than that on the top of PAN. This improvement occurred due to more uniform active layers deposited on HPAN as a result of better interaction between carboxylate group of HPAN with amine group of MPD. Even though the interaction was better, in general, the active layer was still found to be insufficiently dense and selective towards NaCl so the rejection was still lower than IP PA TFC. The extent of uniformity then was further increased by additional interlayers. PEI/PAA interlayer on the top of HPAN showed by far the best performance. This was due to more carboxylate groups provided by PAA as the outermost layer prior to the deposition of MPD/TMC. Carboxylate groups of PAA will serve as seeding sites for subsequent deposition of MPD/TMC. The membrane with PEI/PAA interlayer showed remarkable results, that is, rejection of 98.7% coupled with water flux of 20.7 $\text{L/m}^2\cdot\text{h}$ which is 75% higher than IP PA TFC (the membrane was tested at pressure of 15.5 bars and NaCl concentration of 2000 ppm). This is indeed a very promising result in the field of RO.

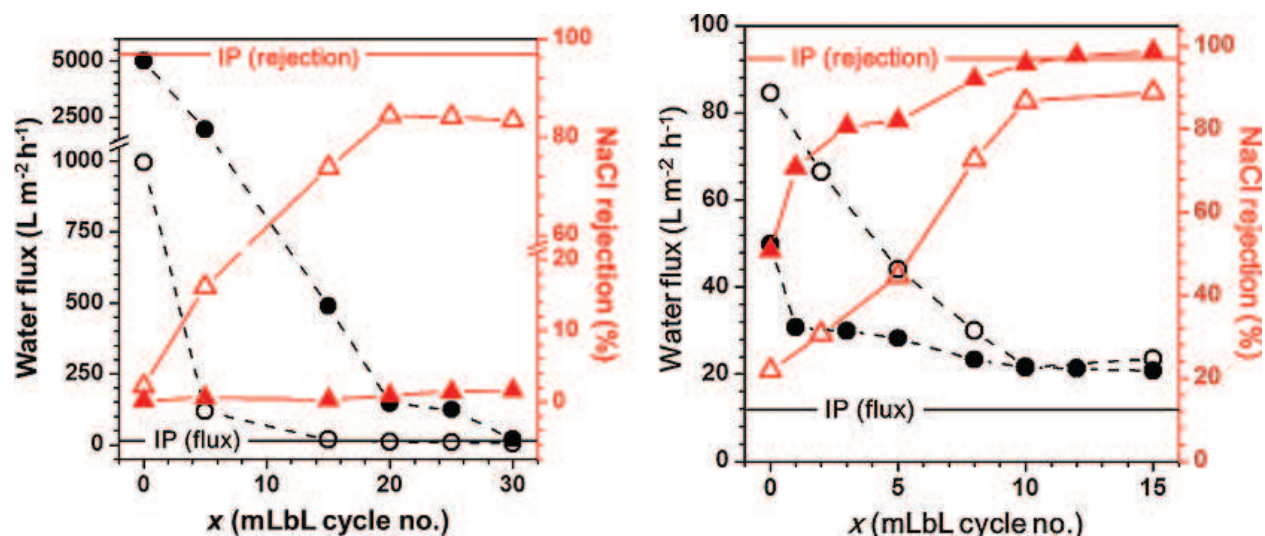


Figure 8. m-LbL PA TFC performance (represented by a circle for water flux and triangle for rejection). PAN support (left figure, filled symbol), HPAN (left figure, unfilled symbol), PEI/PAA-HPAN support (right figure, filled symbol) and PEI-HPAN (right figure, unfilled symbol) (adapted from Ref. [62]).

3.2. Membrane modification

In this section, the use of LbL assembly to modify the surface of existing RO, NF or FO membranes will be discussed. One of the most important surface modification purposes is to protect the membrane from being directly exposed to harsh environment such as chlorine or oxidants content in water, foulants and pH of the water at which the membrane life will be shortened. There have been tremendous works in the modification of commercially available membranes using different approaches such as coating, blending, incorporating nanomaterials, functionalization, grafting, etc. [63]. This section is devoted only for membrane modification using LbL assembly, which is mostly a sort of coating technique that can be simply a physical process or chemically bonded to the membrane surface.

The idea behind modification of the RO membrane using LbL is basically to alter surface properties that can reduce fouling tendency for example by reducing the roughness and hydrophobicity. The study showed that additional LbL films improve, significantly, the smoothness of the surface, improve salt rejection but sacrifice the flux. However, as far as fouling is concerned, this surface modification is very promising as no flux decrease was noticed when the membrane was exposed to foulants containing water [64].

Recently, graphene oxide (GO), a single-sheet functionalized graphene with oxygen-rich functional group, has attracted attention from researchers in the field of water treatment. This material provides fast water transport, hydrophilicity as well as excellent chemical stability. The main objectives of employing GO or GO/polyelectrolyte are to improve chlorine resistance and reduce the bio-fouling without sacrificing the flux (see Figure 9 for the schematic illustration of GO-modified membrane) [65, 66]. Biofouling test using bovine serum albumin (BSA) showed that GO-modified PA TFC membrane can maintain the flux constant after approximately 6 h of testing; meanwhile, pristine PA TFC membrane kept showing

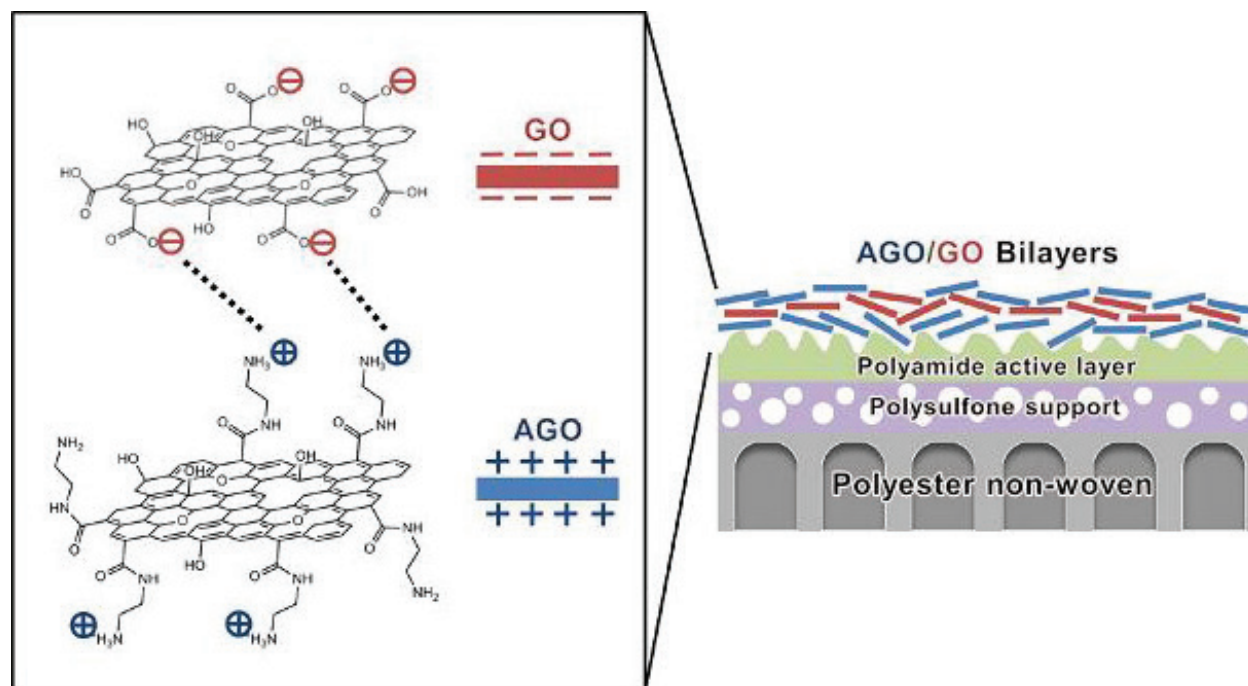


Figure 9. A schematic illustration of a multilayer GO on PA TFC membrane (adapted from Ref. [65]).

linear flux reduction even after 12 h of testing. This result showed that GO-modified PA TFC improves the fouling resistance but does not completely remove the fouling as indicated by flux decrease for the first 6 h of the experiment [65].

4. Conclusion and future work

IP PA TFC membrane has been extensively used in the area of RO, NF and FO. However, the nature of the process as well as the properties of the polyamide creates several problems such as chlorine and fouling resistance that are likely difficult to solve as long as the same fabrication technique is used. This is because the IP itself does not provide fine control over the film properties, not to mention its limited applicability only to few types of polymers such as polyamide and polycarbonate. Meanwhile, polyamide itself is naturally hydrophobic which causes severe fouling problems and has weak resistance against chlorine and oxidants. Relatively new technology, LbL assembly, offers flexibility and great control over the film properties which are the main keys to overcome aforementioned problems associated with PA TFC.

Based on literature study, most of the work in LbL desalination membrane still focuses in employing polyelectrolyte to form an active layer. Meanwhile, it has been investigated that many polyelectrolytes are highly hydrophilic in nature, they swell a lot when exposed to water and even swelling can be aggravated by salt infiltration [67] while those are two main compounds in saline water. Some attempts have been done to maintain stability of polyelectrolyte such as heat-induced, chemical or UV light crosslinking. However, only few

studies have been done to investigate long-term stability of those membranes and even to the best of our knowledge most of studies were done under very soft conditions such as low salt concentration, typically 1000–2000 ppm. Thus, testing in harsh conditions for example at NaCl concentration of 32,000 ppm for longer duration must be done particularly for those LbL membranes intended to be used in RO or FO applications. The result of this study will definitely drive the research in finding the best protocol to create the most stable LbL membrane.

Also, from literature study, we found that most of the works were done using traditional dip-LbL. This method is quite difficult to be brought to an industrial scale as the adsorption process limited by diffusion of polyelectrolyte onto the support surface is a time-consuming process. Several researchers have migrated to other LbL assemblies such as dynamic LbL, semi-dynamic LbL, Sr-LbL and SA-LbL that utilize external force to speed up the adsorption process. Surely, more extensive works are urgently required for those LbL assemblies.

One of the advantages of LbL assembly that has not been thoroughly observed was the flexibility and applicability of this technique to create ultra-thin films from various materials. To the best of our knowledge, most of the works are still focused on polyelectrolyte. It is true some researchers have started introducing some inorganic nanomaterials such as silver nanoparticles, graphene oxide and clay, but still there is huge space available to do research in terms of membrane material. There were many polymers that have never been investigated because no appropriate technology was applicable to prepare ultra-thin films using those polymers. After the rediscovery of LbL, the door has opened. Using LbL assembly, one can create the film either from the polymer itself or from the monomers as in the case of m-LbL. One can also combine organic and inorganic materials with nano-level control easily to fabricate highly resistant membranes towards chlorine and foulants and, at the same time, give high flux and high rejection or selectivity for instance. Tailoring the film properties is one of the strength and advantages of LbL assembly that has not been deeply investigated but for preparing separation membrane.

As a new emerging technology, LbL must still go a long journey; it is going to face many challenges in the future. However, with all of its strength, versatility and robustness, we believe that LbL membrane one day will dominate the desalination membrane just as IP PA TFC did in the last couple of decades.

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