

PRESSURE DRIVEN CONDUCTING POLYMER MEMBRANES DERIVED FROM LAYER BY LAYER FORMATION AND CHARACTERIZATION: A REVIEW

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Abstract

The layer-by-layer method is a technique used for the fabrication of ultra-thin defect free films which involves alternating sequential adsorption of polycations and polyanions, while conducting polymer is characterized by a conjugated structure of alternating single and double bonds. The use of layer-by-layer in producing a membrane for separation has received considerable interest due to its properties. However, the introduction of conducting polymer as a base membrane is relatively new. Therefore, in this review, we discuss in detail three types of LBL techniques (dip, spin and spray layer-by-layer) along with their parameters. We will also summarize current developments on the characterization of modified membrane prepared using the layer-by-layer techniques in terms of morphology, physical and chemical properties, and separation performances.

Keywords: Membranes, conducting polymer, polyelectrolytes, characterization.

1. Introduction

Membrane-based technologies are the leading technology for all kinds of separation techniques due to its intrinsic characteristics such as operational simplicity, environmental impact, high selectivity and permeability for the transport of specific components [1]. A membrane is an interphase between two adjacent phases acting as a selective barrier that regulates the transport of substances between the two compartments. Membrane separation technologies refer to any separation processes in which membranes function as both a barrier and a sieve for separating feed species such as liquid mixtures, gas mixtures, and colloidal particle mixtures [2]. The main advantages of membrane technology

Abbreviations	
AFM	Atomic Force Microscopy
CA	Cellulose Acetate
CP	Conducting Polymer
D	Dialysis
ED	Electrodialysis
FESEM	Field Emission Scanning Electron Microscopy
FO	Forward Osmosis
GS	Gas Separation
LBL	Layer-by-layer
MF	Microfiltration
NF	Nanofiltration
P4VP	Poly(4-vinylpyridine)
PA	Polyacetylene
PAA	Polyacrylic Acid
PAH	Poly(allylamine hydrochloride)
PAN	Polyacrylonitrile
PAni	Polyaniline
PDDA	Poly(diallyldimethylammonium chloride)
PEI	Poly(ethyleneimine)
PES	Polyethersulfone
PET	Polyethylene terephthalate
PN	Polyacrylonitrile
PP	Polypropylene
PPy	Polypyrrole
PS	Polysulfone
PSF	Polysulfone
PSS	Poly(styrenesulfonate)
PTh	Polythiophene
PV	Pervaporation
PVDF	Polyvinylidene Fluoride
PVM	Polyvinylamine
PVS	Poly(vinylsulfate)
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
THF	Tetrahydrofuran
UF	Ultrafiltration
XPS	X-ray Photoelectron Microscopy

compared to other unit operations in chemical engineering relate to this unique separation principle, i.e., the transport selectivity of the membrane. Separations with membranes do not require additives, and they can be performed isothermally at low temperatures, and at low energy consumption compared to other thermal separation processes. Also, the up scaling and downscaling of membrane processes as well as their integration into other separation or reaction processes are easy [3]. It also holds a significant commercial impact in several areas, including water and wastewater treatment, chemical, metallurgical and petrochemical-related industries, food industries and bio-separation areas [1].

There is a variety of classifications of membrane processes for separation such as dialysis (D), electrodialysis (ED), pervaporation (PV), gas separation (GS), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO) [3, 4]. They can be prepared using ceramic and polymeric materials [5]. There are many studies that have shown that ceramic materials have several advantages over polymeric materials. For example, membranes from ceramic materials are highly stable in terms of chemical and thermal stability. Unfortunately, the market share of polymeric membranes is far greater than ceramic membranes as polymeric materials are easier to process and are less expensive [6]. Instead of those materials discussed, there are also membranes from inorganic materials that have been successfully applied in the dehydration of tetrahydrofuran (THF). Inorganic membranes consist of oxides or metals and can be present in multi-layer supporting structures, or as self-supporting structures. They can operate in harsh conditions and be highly selective and permeable for specific molecules [7]. However, to produce an inorganic membrane requires high costs compared to producing a polymeric membrane although its system design is more complex [8]. Therefore, the usage of polymeric membranes in separation could be a highly promising platform for the development of an efficient and sustainable separation technique.

2. Polymer Membranes

Numerous interesting scientific and technological challenges are presented by the area of polymeric membranes in separation techniques. There are many polymers available but to make the selection on the materials of the polymer membrane is not an easy task and cannot be overstated. The most common polymers used in membrane synthesis are polysulfone (PS), polyethersulfone (PES), polyacrylonitrile (PN), polypropylene (PP), polyvinylidene fluoride (PVDF) and cellulose acetate (CA) [5]. An overview of the polymers as materials for industrially established separation membranes is shown in Table 1.

A closer inspection reveals that most membranes currently on the market are based on relatively few polymers which had originally been developed for other engineering applications. With the selective membrane as the key element, the contributions of polymer chemistry, physics, and engineering are very important. Furthermore, from the analysis of the activities in different areas, it is shown that advanced polymer membranes will often be based on tailored functional macromolecular architectures instead of just 'bulk polymer' properties [3].

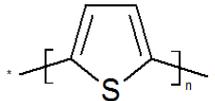
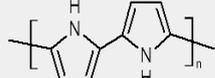
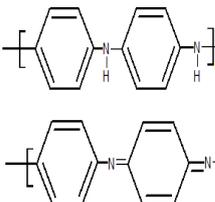
2.1. Conducting polymer membranes

Conducting polymers (CP) are a special class of polymeric materials with electronic and ionic conductivity. It can be used in both dry or wet states owing to its electronic conductivity, porous structure or because of its process-ability in micro-structuring processes [9]. The most commonly studied classes of conducting polymer are polyacetylene, polythiophene, polypyrrole and polyaniline [10]. Table 2 shows their properties, structure and common preparations.

Table 1. Polymers as materials for industrially established separation membranes [3].

Polymer	Morphology			Membrane process
	Barrier type	Cross-section	Barrier thickness (μm)	
Cellulose acetates	Nonporous	Anisotropic	~0.1	GS, RO
	Mesoporous	Anisotropic	~0.1	UF
	Macroporous	Isotropic	50-300	MF
Cellulose nitrate	Macroporous	Isotropic	100-500	MF
	Mesoporous	Anisotropic	~0.1	UF, D
Cellulose, regenerated	Nonporous	Isotropic	50-500	ED fuel cell
Perfluorosulfonic acid polymer	Nonporous	Anisotropic	~0.1	UF
Polyacrylonitrile	Mesoporous	Anisotropic	~0.1	UF
Polyetherimides	Mesoporous	Anisotropic	~0.1	UF
Polyethersulfones	Mesoporous	Anisotropic	~0.1	UF
Polyethylene terephthalate	Macroporous	Isotropic	50-300	MF
	Nonporous	Isotropic	6-35	MF
Polyphenylene oxide	Nonporous	Anisotropic	~0.1	GS
Poly(styrene-co-divinylbenzene), sulfonated or aminated	Nonporous	Isotropic	100-500	ED
Polytetrafluoroethylene	Macroporous	Isotropic	50-500	MF
Polyamide, aliphatic	Nonporous	-	~0.1	GS
	Macroporous	Isotropic	100-500	MF
Polyamide, aromatic	Mesoporous	Anisotropic	~0.1	UF
Polyamide, aromatic, in situ synthesized	Nonporous	Anisotropic/composite	~0.05	RO, NF
Polycarbonates, aromatic	Nonporous	Anisotropic	~0.1	GS
	Macroporous	Isotropic	6-35	MF
Polyether, aliphatic crosslinked, in situ synthesized	Nonporous	Anisotropic/composite	~0.05	RO, NF
	Macroporous	Isotropic	50-500	MF
Polyethylene	Nonporous	Anisotropic	~0.1	GS, NF
Polyimides	Macroporous	Isotropic	50-500	MF
Polypropylene	Nonporous	Anisotropic/composite	~0.1 < 1-10	GS PV, NF (organophilic)
Polysiloxanes	Nonporous	Anisotropic	~0.1	GS
Polysulfones	Nonporous	Anisotropic	~0.1	GS
	Mesoporous	Anisotropic	~0.1	UF
Polyvinyl alcohol, crosslinked	Nonporous	Anisotropic/composite	< 1-10	PV (hydrophilic)
Polyvinylidene fluoride	Mesoporous	Anisotropic	~0.1	UF
	Macroporous	Isotropic	50-300	MF

Table 2. Commonly studied classes of CP .

Name and structure	Properties	Preparation	Ref.
Polyacetylene (PA) 	<ul style="list-style-type: none"> •Continuous solid films with densities of 1.05-1.10. •Controlled morphology range: amorphous, semi-crystalline and crystalline. •Film can be stretched during or prior to conversion. •Conductivity ranges 10^3-$1.7 \times 10^5 \text{ Scm}^{-1}$. 	<ul style="list-style-type: none"> •Electrochemical •Chemical synthesis 	[9, 11]
Polythiophene (PTh) 	<ul style="list-style-type: none"> •Good electrical conductivity and optical property. •Conductivity ranges 10-10^3 Scm^{-1}. 	<ul style="list-style-type: none"> •Electrochemical •Chemical synthesis 	[9, 12]
Polypyrrole (PPy) 	<ul style="list-style-type: none"> •Opaque, brittle and amorphous materials. •Conductivity ranges 10^2-$7.5 \times 10^3 \text{ Scm}^{-1}$. 	<ul style="list-style-type: none"> •Electrochemical •Chemical synthesis 	[9, 11]
Polyaniline (PANI) 	<ul style="list-style-type: none"> •Belongs to the semi-flexible rod polymer family. •Requires simple doping/dedoping chemistry. •Exists as bulk films or dispersions. •Conductivity ranges 5-200 Scm^{-1}. 	<ul style="list-style-type: none"> •Electrochemical •Chemical synthesis 	[9, 12]

The interest on CP as membrane materials have increased due to its unique characteristics. Electrically, CP has been described as a new class of 'synthetic metals' which had reached high interest in the past few years. Its usage was confirmed by the 2000 Nobel Prize in chemistry for the discovery and development of conducting polymers [10]. CP is characterized by a conjugated structure of alternating single and double bonds. The feature shared by all of them originates from the common nature of their π -electron system which gives enhanced conductivity in oxidized or reduced state, and can go through reversible redox activation in a suitable environment [13].

2.2. Modification of polymer membrane

The membrane process conditions must be engineered very carefully, but the performance limits are clearly determined by the membrane itself. The current membrane polymers used are biopolymers (mainly cellulose derivatives) or (less

than 20 major) synthetic engineering polymers which had originally been developed for different purposes. The development of synthetic membranes had always been inspired by the fact that the selective transport through biological membranes is enabled by highly specialized macromolecular and supramolecular assemblies involved in molecular recognition [3]. Recent advances in membrane technology have become the focus of membrane development which is the key determinant of separation performance and water productivity.

The materials used in the membrane production are generally constructed from durable PS and its derivatives, the majority of which are hydrophobic. Due to the hydrophobic nature of PS material, conventional PS membranes easily suffer serious membrane fouling and have low permeation flux, making it undesirable in the long-lasting filtration process [1]. Membrane fouling refers to the blockage of membrane pores during filtration by the combination of sieving and adsorption of particulates and compounds onto the membrane surface or within the membrane pores. Pore blockage reduces the permeate production rate and increases the complexity of the membrane filtration operation. This is the most challenging issue for further membrane development and applications [14]. Fouling can be classified into 4 major categories which are organic fouling, colloidal fouling, scaling and biofouling. Table 3 briefly describes each fouling phenomena and their common foulants that contribute to the problems.

As a consequence, the surface of these membranes must be rendered hydrophilic through the addition of wetting agents, e.g. hydrophilic polymers and/or by chemical modification of the membrane structure prior to be used in aqueous separations. The approaches currently used for membrane surface modification include surface graft polymerization, exposure to irradiation, interfacial polymerization, chemical cross-linking, polyelectrolytes coating, etc. [1]. This is because single component materials, no matter natural or synthesized, can hardly fulfill all of the requirements for making an ideal separation membrane. On the other hand, multi-component composite materials can combine the advantages of different components and achieve optimum properties and performance [2].

In the area of membrane separation, the (layer-by-layer) LBL method seems to be ideally suited to provide accurate control over the film's thickness on a nanometre-scale. Importantly, such LBL films are free of defects that may be detrimental for separation efficiency. By far, polyelectrolytes has proven to be a versatile and simple method for the fabrication of very thin polyelectrolyte multilayers, making it highly suitable for the preparation of polyelectrolyte CP membranes for separation [15].

3. LBL Self-assembled Polyelectrolytes

Polyelectrolytes are polymers carrying either positively or negatively charged ionizable groups. In polar solvents such as water, these groups can dissociate, leaving charges on polymer chains and releasing counter ions in solutions [16]. Such dissociation is typically accompanied by smaller oppositely charged counter ions that tend to neutralize the charge on the repeating units of the macromolecule, preserving its electro-neutrality. A polyelectrolyte in

low ionic strength solutions tends to be in its most extended and uncoiled form due to the intermolecular repulsion of the macromolecule. On the other hand, when the ionic strength of the solution is increased, polyelectrolytes tend to become more coiled due to the screening effects of polymer charges by the excessive presence of smaller salt counter ions in solution [17]. They are referred to as strong polyelectrolytes if they contain permanent charges and, thus, fully dissociate in water. In contrast, the charges and charge dissociation of weak polyelectrolytes can be partial and strongly dependent on pH [15].

Polyelectrolytes' complexation can be formed when one polyelectrolyte interacts with an opposite charged polyelectrolyte. There are many polyelectrolytes with different charges, structures and properties [18]. Figure 1 shows the chemical structures of common polyelectrolytes. Polyelectrolytes are classified according to their origin, either standard synthetic polyelectrolytes or natural polyelectrolytes [19]. Combining two or more polyelectrolytes either as a multilayer or as a complex enables one to obtain various materials (of precisely defined properties), which are the same as the polyelectrolytes in terms of physical structure and morphology [20].

Table 3. Fouling phenomena and common foulants [21].

Type of fouling	Definition	Foulants
Organic fouling	Deposition or adsorption of dissolved or colloidal organic material on the membrane surface.	<ul style="list-style-type: none"> • Natural organic matters • Effluent organic matter • Proteins • Polysaccharides.
Colloidal fouling	Accumulation of retained colloidal and particulate matter on the membrane surface.	<ul style="list-style-type: none"> • Clay minerals • Colloidal silica • Metal oxides (iron, aluminium and manganese) • Organic colloids • Suspended matter and salt precipitates
Scaling	Ionic product of a sparingly soluble salt exceeds its equilibrium solubility product and precipitates and forms a scaling layer on the membrane surface.	<ul style="list-style-type: none"> • Calcium sulfate • Calcium carbonate • Barium sulfate • Silica scale
Biofouling	Adhesion and growth of microorganisms (bacterial cells or microbial flocs) accompanied with agglomeration of extracellular materials on the membrane surfaces.	<ul style="list-style-type: none"> • Bacteria • Fungi

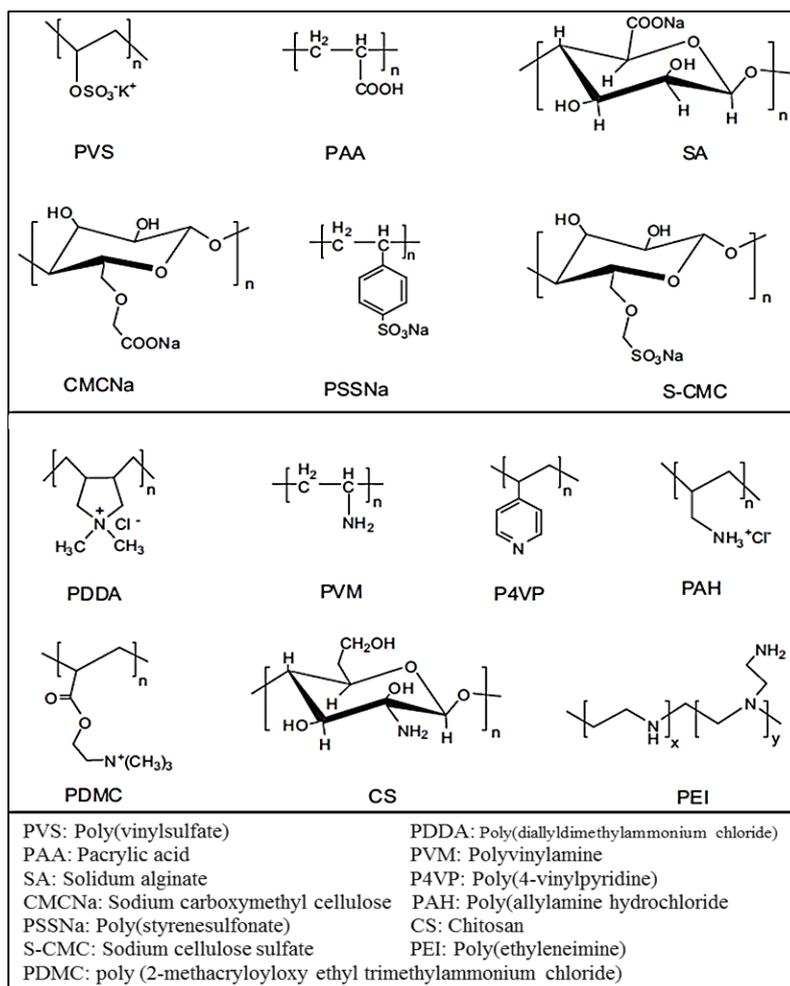


Fig. 1. Chemical structures of common polyelectrolytes and abbreviations [2, 18].

3.1. Layer-by-layer polyelectrolytes

The LBL method is a technique for the fabrication of ultra-thin defect free films with tailored composition and tuneable properties which involves alternating sequential adsorption of polycations and polyanions on a charged surface followed by a rinsing step after each adsorption to remove weakly associated polymer chains [13]. LBL deposition was reported first by Iler (1996) more than 40 years ago. It has been explored and developed as a thin film for deposition and surface modification processes, especially during the last twenty years [22]. Sequentially, Decher and Hong in year 1991 has explored the LBL self-assembly as a new approach in material science and engineering, and since then, this technique has attracted great attention for various potential applications [15, 19].

LBL techniques

The LBL self-assembly can be achieved through four simple steps as shown in Fig. 2. For the purpose of illustration, a charged substrate is considered as a negative charge [19].

Step 1: Polycations will be adsorbed on the negative charged surface of the substrate due to electrostatic attraction;

Step 2: Wash the substrate surface with de-ionized water in order to remove excess polycation molecules which are not strongly adsorbed on the surface;

Step 3: Immerse the substrate into a polyanion solution, where the negative charges will be adsorbed onto the surface;

Step 4: Repeat the above steps and a polyelectrolyte multilayer will be formed.

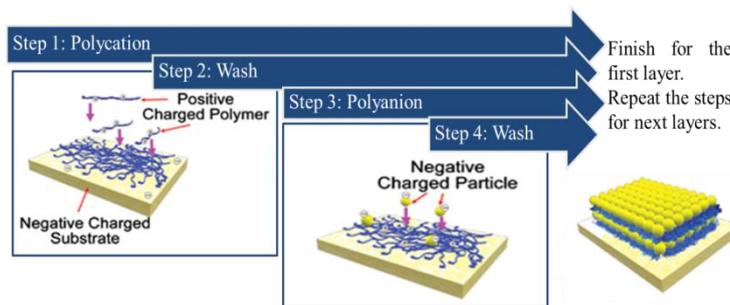


Fig. 2. Schematic diagram of LBL assembly [18, 23].

The LBL coating can be performed using various methods, such as dip-LBL, spray-LBL, and spin-LBL, with dip-LBL being the most commonly used method. The main advantages of the alternative methods (spray/spin-LBL) are that lower amount of liquids are needed to coat large surface areas, as well as a significant reduction in processing time [15]. In this section, these different production methods will be briefly addressed.

a) Dip-LBL

The most common and simple method is dip-LBL. The practical set-up of this method is extremely simple as described previously; at each time, the substrate is dipped into the polyanion and polycation solutions, and then the substrate is rinsed with plenty of water between these two steps [16, 20]. These deposition procedures are then cycled to obtain the desired number of bilayers and the multilayered films are dried under nitrogen gas purging at the end of their fabrication [24]. The dip-LBL process is efficient, but the overall long deposition time and rinsing steps make it a very time-consuming method. However, multilayers prepared by this process are thicker, denser and smoother compared to the other processes [15, 24].

b) Spin-LBL

Spin-LBL, as reported by Chiarelli [15], is formed by dropping cationic and anionic aqueous solutions onto a spinning substrate. It was claimed that this

dynamic technique, to some extent, is better than the traditional method because a good flux could be obtained, has fast deposition and only small amounts of liquids are needed to coat large surface areas [17, 22]. In principle, there are four distinct stages to the spin-coating process. The first stage is the deposition of the coating fluid onto the substrate. The second stage is when the substrate is accelerated up to its final and desired rotation speed. The third stage is when the substrate is spun at a constant rate and fluid viscous forces dominate the fluid thinning behaviour. Finally, the fourth stage is when the substrate is spun at a constant rate and solvent evaporation dominates the coating thinning behaviour. Because of this spinning process, different adsorption mechanisms occur in the dip-LBL and spinning methods [24].

c) Spray-LBL

In spray-LBL, the PEs solutions and rinsing solutions are sprayed over the substrate in turn. The rinsing step has been expelled through constant drainage to remove the excess of material that is sprayed onto the surface [17]. The influence of various parameters such as spraying time, polyelectrolyte concentration, and effect of film drying during multilayer construction must be considered. Because drainage constantly removes a certain quantity of the excess materials arriving at the surface, one can even skip the rinsing step and, thus, speed up even further the whole build-up process. The spraying method is convenient, fast, and more generally applicable for the coating of large surfaces besides providing homogeneous films over large areas [15].

To summarize all the static assembly methods, Fig. 3 shows the three common LBL methods applied for various applications. Beside static assembly, there is another type of method in LBL called dynamic assembly. The dynamic assembly method is done by using membrane cells such as dead-end cells [25-27] or other equipment [28] which can hold the membrane so that the single sided LBL could be applied onto the membranes. Besides allowing for the reduction of deposition cycles [27], the dynamic assembly method could also improve membrane permeability [29] by filtrating the polyanion and polycation alternatively during a pre-determined period of filtration to allow polyelectrolytes to integrate within the pore structure of the membrane. Figure 4 below shows the summarization of the advantages and disadvantages of both the static and dynamic assembly LBL techniques.

Factors affecting the LBL

In the membrane separation areas, there are different process parameters that can be used to tune the properties of the deposited polyelectrolyte layers and the multilayer structure. The formation of a polyelectrolyte multilayer self-assembly is usually reliant on the electrostatic adsorption between the substrate and the subsequent layers [30]. Like a chemical reaction, the precise structure of each layer and the properties of the whole film depend on a set of control parameters such as ionic strength, pH, and washing and drying temperatures [15, 19, 31]. Stated below are the explanations for some parameters, but in general the processing window is rather broad. Polyelectrolyte multilayer films are often independent of the underlying substrate. However, the influence of the substrate is typically lost after a few deposition cycles [31]. Since the polyanion and

polycation adsorptions are often repeated consecutively, each polyanion adsorbs onto a polycation covered surface, and vice versa. After a few layers, the structure and properties of each layer are often governed by the choice of the respective polyanion/polycation pair and by the deposition conditions.

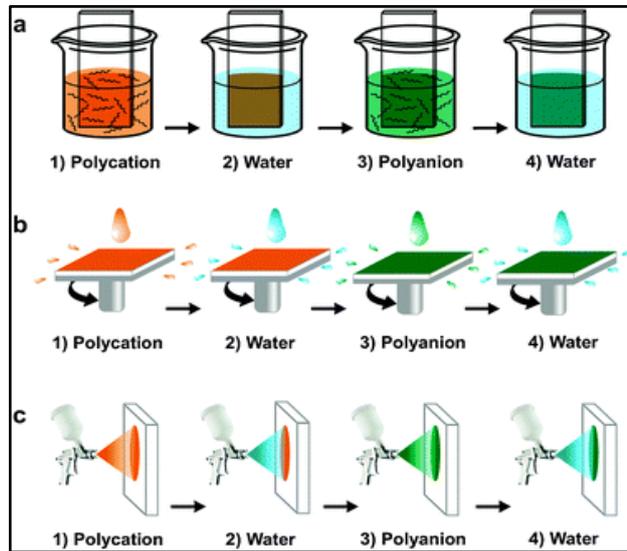


Fig. 3. Three different LBL techniques for various applications. a) Dip-LBL b) Spin-LBL c) Spray-LBL [32].

Layer-by-Layer Polyelectrolyte Technique			
Static Assembly		Dynamic Assembly	
Dip-LBL	Spin-LBL	Spray-LBL	Membrane cell
Advantages			
<ul style="list-style-type: none"> - Simple method - Very efficient - Film produce more thicker, dense and smoother. 	<ul style="list-style-type: none"> - Fast deposition - Small amount polyelectrolytes - Film produce more uniform and smooth. 	<ul style="list-style-type: none"> - Fast deposition - Applicable for large area. 	<ul style="list-style-type: none"> - Polyelectrolytes could integrate within the pores. - Reduces numbers of layers.
Disadvantages			
<ul style="list-style-type: none"> - Time consuming - Risk of cross-contaminate 	<ul style="list-style-type: none"> - Complex method - Applicable only for small area 	<ul style="list-style-type: none"> - Numbers of parameter must be considered 	<ul style="list-style-type: none"> - Complex method - Time consuming

Fig. 4. Advantages and disadvantages between static and dynamic assembly LBL techniques.

a) Ionic strength

The ionic strength of polyelectrolyte solutions plays a key role in the formation, stability, structure and properties of polyelectrolyte multilayers. Generally, an increase in ionic concentration results in an increase in film thickness due to the polyelectrolyte charge compensation, resulting in a more globular rather than extended polyelectrolyte structure. However, with the diffusion of polyelectrolytes into the interior or if interactions between the adsorbing polyelectrolyte and the interior takes place, the film's thickness increases exponentially [19]. In contrast, the decreased solubility of polymer chains in salt solutions will enhance the stability of the polyelectrolyte multilayer once formed, since weakly interacting ions enhance the hydration of polymer chains which lead to smoother and thinner polyelectrolyte multilayers [15].

b) pH

pH provides numerous possibilities to control the structure of multilayer films. A change in the pH of the solutions will alter the dissociation of polyelectrolytes and ions, which will alter the successive adsorption steps. Similarly for ion concentration, a change in pH value also results in a linear or exponential growth of film layers for weak polyelectrolytes dependent on a charge density mismatch under defined pH conditions [19]. For solvents, relatively little work has been done in this area. However, it has been reported that the addition of an organic solvent to the polyelectrolyte solutions also influences the polyelectrolytes' multilayer growth. For example, increasing alcohol content in aqueous adsorption solutions increases the strength of the electrostatic interactions between polyelectrolyte chains due to the decreased dielectric constant of the solvent mixture. Furthermore, the lower solvent quality of alcohol–water mixtures for polyelectrolytes in comparison to water leads to the collapse of polymer chains in more compact structures [15].

c) Washing and drying temperatures

To remove unbound polyelectrolytes and prevent cross-contamination of solutions, coated substrates are washed in good solvents for the polyelectrolytes. Strong polyelectrolyte layers (with high surface charge density) are not significantly altered by the rinsing of the LBL construct since the layer is secured by strong interactions. However, weakly bound polyelectrolytes (low surface charge density) may be stripped off, limiting successful LBL assembly. Next, polyelectrolyte multilayers are allowed to dry after each rinsing step since the successive dipping of the adsorbed films into the respective polyelectrolyte solutions ensures a moist environment and enhances chain flexibility and ionization during the adsorption steps. Therefore, thinner and less dense films are generally formed due to a higher degree of multivalent adsorption [19]. The rinsing volume is important to avoid cross-contamination of deposition solutions. While many multilayer films grow well even without rinsing, one should carefully calculate the required rinsing volumes to avoid cross-contamination in the case of LBL-assembly by dipping [31].

Spontaneous drying under ambient conditions for PAH/PSS films produce more ordered films compared to those dried under nitrogen streaming, which show large disordered regions and can thus influence film structure. Different rates of drying are also dependent on the number of coated layers, especially the

dehydration of the inner layers [33]. Therefore, temperature can affect drying rates and is therefore an important experimental parameter. A higher temperature decreases the enthalpic electrostatic attraction due to an increase in chain mobility and therefore, enhances the entropic gain of the release of solvent molecules and counterions. Higher chain mobility leads to an increase in the number of loops and tails that stick into the solution above the LBL film by providing the kinetic energy necessary to surmount the barriers to conformational changes [15].

3.2. Application of LBL in various separations and their advantages

The LBL self-assembly methods have advantages compared to the more conventional coating methods, including (1) the simplicity of the LBL process and equipment, (2) its suitability to coating most surfaces, (3) the availability of an abundance of natural and synthetic colloids, (4) the flexible application to objects with irregular shapes and sizes, (5) the formation of stabilizing coats, and (6) control over the required multilayer thickness [19]. Furthermore, LBL assembly provides an inexpensive, cost effective, highly reproducible, environmentally friendly and robust method to build ultra-thin polymer films that are water resistant and stable even at high ionic strength and in acidic and basic media over a wide range of temperatures, pH and solvent changes [17, 34].

The LBL techniques are suitable to be used to improve CP membranes in terms of its morphology, chemical and physical properties, and their performances. The LBL polyelectrolyte technique is usually guided by a driving force of hydrophobic interaction, hydrogen-bond, covalent bonding, and electrostatic interaction between assembled compounds [35]. The adsorption of neutrally, positively and negatively charged polyelectrolytes onto a CP membrane can contribute to the formation of very thin films and at the same time, able to change the properties of the membrane.

The versatility of the multilayer system has generated a wide range of potential applications in different areas, including bioactive materials. Since biomolecules are often electrically charged and the LBL methods work well in dilute aqueous or buffer solutions, it is a promising method to be used for assembling thin films with biological activity. In the field of optical devices, multilayers can be used as anti reflecting films which are easily applied on any type of geometrical object (by immersing the surface in a polyelectrolyte solution to form multilayers) [36].

This technique has also received considerable interest due to its widespread applications such as battery separators, fuel cell membranes, electrically conductive coatings, medical and surgical materials, and chemical sensors and detectors [18]. Besides that, multilayer thin films from LBL also appear in several applications such as antifogging or antireflection coatings and self-cleaning surfaces. The literature also mentions applications in sensor fabrication, friction reducing coatings, integrated optics, and electronic device fabrication. Several industries have benefited from the development and application of this technique, such as the semiconductor, automotive and construction industries [22]. Some new commercial products can be found on the market, e.g. hemocompatible coatings for blood-contacting medical devices, electrochromic visor coating systems, hydrophilization of contact lenses, plastic coatings (Yaza sheets) for

keeping vegetables and fruits fresh for weeks, and free standing electrically conductive elastomeric nanocomposite films (metal rubber) [36].

4. LBL on Conducting Polymer Membranes and Its Properties

In the membrane research field, membrane characterization analyses are important. A variety of techniques and approaches are routinely used for characterizing the physical and chemical properties of membrane surfaces. Membrane surface morphology characterization is also one of the indispensable components of membrane research. However, it relies on rather exhaustive sample preparation procedures and a thorough understanding of the properties of the sample material. In this section, current developments to characterize modified membrane prepared using the LBL technique are summarize in terms of morphology, physical and chemical properties, and separation performance.

4.1. Morphological properties

There are a number of methods that can be used to specify membrane morphology. The classical way of characterizing a membrane is to determine the pore size and distribution of the membrane. The pore sizes determined by different methods do not necessarily agree with each other, but they usually show some common trends. Some of the equipment usually used are the Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray photoelectron microscopy (XPS) [6]. Figure 5 shows the examples of cross-sectional membranes obtained from SEM images.

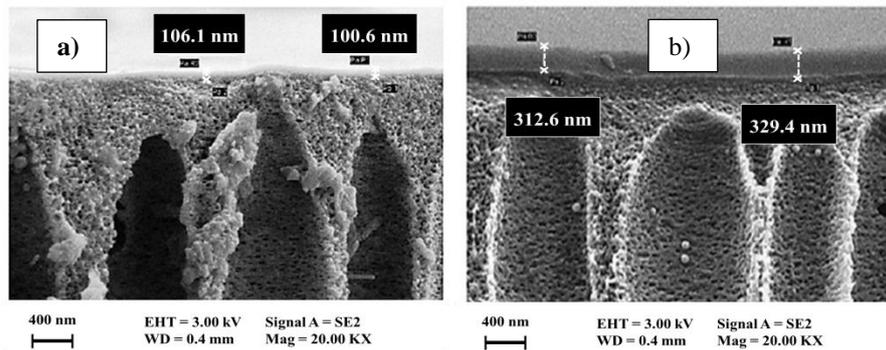


Fig. 5. Cross-sectional FESEM images for membrane modified with one monolayer of PDDA (a) and membrane modified with 5 bilayers of PDDA/PSS (b) [37].

A selective NF membrane-engineered LBL from PDDA and PSS polyelectrolytes were reported by Ng et al. (2014). They stated that the molecular weight of the polyelectrolytes used is an important and influential parameter that affects the bi-layers thicknesses. When high molecular weight polyelectrolytes were used, the thicknesses obtained were several folds greater than those obtained using low molecular weights if the number of bi-layers remained the same. In their research, cross-sectional images from Field Emission Scanning Electron Microscopy (FESEM)

displayed that the membranes were in asymmetric morphologies, with finger-like pores linked by spongy walls. When modified with a single monolayer of PDDA, the average thin film thickness measured was 103.30 ± 4 nm. When modified with 1 bilayer of PDDA/PSS, the thin film thickness measured increased to around 145.15 ± 8 nm. Finally, when 5 bilayers of PDDA/PSS were deposited onto the membrane surface, the thin film thickness increased to 321.00 ± 12 nm [37].

Shi et al. (2013) reported on composite polyelectrolyte multilayer membranes fabricated by using the LBL assembly technique for oligosaccharides' NF separation. Specifically, the chitosan/PSS multilayers designated as the middle layer were first deposited on the hydrolyzed polyacrylonitrile (PAN) UF membranes. Then, the PAH/PSS multilayers designated as the top layer were deposited on the middle layer to form composite polyelectrolyte multilayer membranes. The membrane was layered to 5 bilayers. The cross-sectional images of the PAN membrane via phase inversion and hydrolyzed PAN membranes showed loosely opened pores and finger-like pores for both of the membranes. This indicate that the porous support layer remained intact after hydrolysis. The PAN and hydrolyzed PAN membranes both also exhibited smooth surfaces, while the polyelectrolyte multilayer membranes showed rougher surfaces. Specifically, at 5 bilayers, (PAH/PSS) membranes displayed much smoother surfaces than (chitosan/PSS) membranes which might result in less fouling propensity [25].

4.2. Chemical and physical properties

A variety of techniques and approaches are routinely used for characterizing the physical and chemical properties of membrane surfaces. The measurement of the contact angle formed when a droplet of water is placed on the membrane surface is used to quantify the hydrophobicity/hydrophilicity of the membrane surface. It is now widely accepted that the specific flux rate increases with the increase in hydrophilicity of the material that makes up the membrane. Similarly, hydrophilic and smooth membrane surfaces tend to be less prone to severe fouling events [38].

Contact angle is affected by the diffusion and stretching of the hydrophilic ends of the polymer from the bulk to the surface, which rely on the polyelectrolyte solution's ionic strength and other constraints. According to Ng et al. [37], the unmodified membranes displayed an average contact angle of $43.7 \pm 1^\circ$, while the PES membrane surface modified with PDDA and PSS as the terminating layer have reduced its contact angle value from $44.0 \pm 3.4^\circ$ to $41.4 \pm 2^\circ$. This confirms that the desired membrane surface hydrophilicity can be easily manipulated through salt concentrations in the polyelectrolyte solution. PDDA contains quaternary ammonium compounds that have hydrophobic character and thus, repel water [39]. However, the presence of polar sulfonate groups in PSS enhances the degree of hydrophilicity of the molecules and its anionic character over a wide range of pH values which impart enhanced water absorption and transport characteristics to polymers [40]. Besides, the air bubble contact angle increases as the layer number increases, which means that the hydrophilic properties increase as the number of layers increase [41].

Furthermore, membrane surface roughness was confirmed to be also affected by the solution's ionic strength [42]. Current work reported by have shown that the changes in membrane surface roughness is affected by the number of

polyelectrolyte layers. Unmodified membrane possess the highest surface roughness. It is postulated that polyelectrolytes used during the self-assembly process form complexes to smoothen the substrate. Membranes deposited with more polyelectrolyte layers display lower surface roughness, which suggest that the polyelectrolyte multilayers improve the surface's regularity and uniformity [37]. This theory was agreed also by Ishigami [41]. Their research showed that after 6 bilayers, the membrane surface is covered with a thin layer. As the number of layers increases to 12, the multilayered surface is further covered with polyelectrolytes and the valley parts of the rough morphology are filled in with the deposition. However, the thickness increment per polyelectrolyte layer is not exactly constant, which can be explained by a different surface roughness [43], which increases with the increase in bilayer number. A rough surface has a higher surface area with more available charges than a smoother one. As a consequence, more polyelectrolytes of the opposite charge are needed to compensate for the charges [42].

Slow diffusion of solvents into polymer chains causes a swelling phenomenon and leads to swollen polymeric membranes. Unlike non-polymeric materials, polymers do not dissolve instantaneously, and the dissolution is controlled by either the disentanglement of the polymer chains or by the diffusion of the chains through a boundary layer adjacent to the polymer-solvent interface. Different degrees of swelling can be achieved depending on the cross-linking, crystallinity as well as intermolecular forces involved. The choice of materials and their combination can direct the swelling events and make the membrane performance addressable at a macroscopic level [44]. This swelling would be explained by the diffusion of counter ions of the employed salt solution into the multilayer what leads to an extrinsic compensation of the polymer charges. The weakening of the electrostatic interactions between the charged polymeric chains results in a looser structure, and a reversible swelling of the film is observed. At critical salt concentrations, the ionic bonds that hold the layers together tend to break [45]. If the active skin layer and the supporting substrate underneath do not swell in a coordinated manner, a significant stress can be produced at the interface; if the interfacial stress surpasses a "critical point" which depends on the overall complex interaction between the two neighboring materials, the composite structure could disintegrate, and the membrane would become useless. When polyelectrolyte membranes are in contact with aqueous solutions, membrane swelling may occur because the polymer-polymer intermolecular forces are overcome by strong polymer solvent interactions which lead to membrane instability in these solvents. However, if the polymer-polymer intermolecular forces are high enough due to crosslinking, crystallinity or strong hydrogen bonding, then membrane swelling will not be significant [18].

There are some studies on the stability of polyelectrolyte multilayer membranes in different solvents, which showed that membrane performance is shown to change considerably depending on external conditions. Carrière et al. (2004) showed that the swelling of PSS/PAH films is related to the top layer. When the top layer is PAH, the films swell 25% less than those capped with PSS [46]. In addition, Harris & Beuening (2000) reported that the thickness of a membrane with 10 double layers of PSS/PAH increased by 40% if immersed into a pH 6.3 buffer water solution and the membrane thickness was further increased when soaked in a pH 10 buffer water solution due to the swelling of the PSS/PAH multilayer [47]. Even worse, Burke & Barrett (2005) found that PAH/hyaluronic

acid films can reach a degree of swelling as high as 800% in some cases, and had suggested that it is possible to control and tune the swelling behavior of such multilayer assemblies by learning how each parameter of the system influences the hydration capacity of the films [48].

The degree of swelling of polyelectrolyte multilayers depends on both the solvent and the hydrophilicity of the polyelectrolyte. It is well known that water molecules can enter hydrophilic polymer membranes due to their strong affinities, and this generally leads to the swelling of the polymer. Similar to water, ethanol and isopropanol are also quite hydrophilic and thus, these alcohols may swell polyelectrolyte multilayers as well [18]. Poptoshev et al. found that when a PEI/PSS/PAH film is immersed into ethanol solutions, the resulting membrane swelling causes damage in membrane integrity. Besides that, the polyelectrolyte films collapse to the surface as a result of the unfavorable segment–solvent interactions [49]. Ethanol is quite hydrophilic and could enter hydrophilic polymer membranes due to its strong affinities which also generally lead to the swelling of the polymer [18].

4.3. Separation performances

Flux is the flow rate through an individual membrane filter module expressed in terms of gallons of flow per square foot of membrane filter surface area per day. The permeation flux of the membrane may vary depending on the applied pressure, temperature, conversion factor, and feed concentration [50]. Jia Xu et al. (2010) worked on a novel thin-film-composite membrane based on a layer-by-layer self-assembly of polyelectrolytes onto an inter-facially polymerized polyamide membrane for dehydration of ethylene glycol by pervaporation. PEI and PAA were used as the polycations and polyanions, respectively. The resulting membranes showed a good perm selectivity flux with only two to three bilayers of polyelectrolytes with a permeation flux of $0.4 \text{ kgm}^{-2}\text{h}^{-1}$ and a separation factor of 340 obtained at $40 \text{ }^\circ\text{C}$ for a feed water concentration of 3 wt% using a membrane with three polyelectrolyte bilayers. The permeation flux of the membrane increased with an increase in temperature, although there was a reduction in the membrane's permeance. The flux increase with temperature was primarily attributed to the increased driving force for permeation [28].

Toutianoush et al. used polyelectrolyte pairs with high charge densities for separation of alcohol/water mixtures. If a polyvinylamine/polyvinylsulfate membrane was used for ethanol dehydration, the separation factor could reach 700 at a flux of $0.5 \text{ kgm}^{-2}\text{h}^{-1}$. The membrane also showed propanol/water and butanol/water selectivities up to 700 and 3,200 respectively [51]. As for Changquan Qiu et al., water permeability decreased from $77.1 \text{ to } 16.4 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ which indicates that polyelectrolyte layers are able to retain magnesium chloride (MgCl_2) but also introduces additional membrane hydraulic resistance. The deposition of additional PAH/PSS layers resulted in a further decrease in water permeability and increase in solute rejection which clearly demonstrates the potential of LBL membranes for high flux FO applications [52].

Zhang et al. proposed another method for dynamic multilayer deposition using an electric field to enhance the fabrication of polyelectrolyte multilayer membranes from PDDA/PSS, PDDAC/PAA and PEI/PAA on a reverse osmosis

membrane. The pervaporation performance of the polyelectrolyte multilayers for separating isopropanol/water mixtures was better than that of membranes prepared under static self-assembly conditions. Using four PEI/PAA double layers, a separation factor of 1,075 and a permeation flux of $4.05 \text{ kgm}^{-2}\text{h}^{-1}$ were reported at 70°C (Table 4) [53].

Jiafu Shi et al. used chitosan/PSS multilayers designated as the middle layer which were deposited onto hydrolyzed PAN UF membranes. PAN UF membranes were used as the support layer of the multilayer of chitosan PSS. Then, the PAH/PSS multilayers designated as the top layer were deposited on the middle layer to form composite polyelectrolyte multilayer membranes. During the NF separation of oligosaccharides, composite polyelectrolyte multilayer membranes acquire a permeation flux of $3.7\pm 0.3 \text{ Lm}^{-2} \text{ h}^{-1}$, 100% rejection of oligosaccharides and $63.0\pm 0.5\%$ rejection of glucose along with a high maltose/glucose selectivity of 46 (Table 4), demonstrating the promising potential for one-step membrane separation of oligosaccharide mixtures [25].

Krasemann & Tiede (1999) used electrostatic deposition onto a porous PAN/PET substrate (a PET fleece coated with a thin layer of polyacrylonitrile) and showed that the self-assembled polyelectrolytes separation layer is useful to separate gases, liquid mixtures, and ions in liquid solutions. A poly (4-vinylpyridine)/PSS separation layer was shown to have high selectivity for CO_2 and N_2 permeation. For the separation of ethanol/water mixtures, the separation factor could reach 80 when a PAA/PSS separation layer was annealed at temperatures above 60°C (Table 4). Depending on the polyelectrolytes used, the permeation rate of Na^+ could be 15.1 times higher than that of Mg^{2+} in aqueous solutions, which suggested the usefulness of the membranes for ionic separations. Membranes with PAH/PSS separation layers are permeable for monovalent cations, but it rejects divalent cations. The ion separation originates from electrostatic repulsion of the cations by the positively charged parts of the membrane, the rejection being stronger for the divalent than for the monovalent cations because of the higher charge density [23].

5. LBL and CP for Future Membrane

In this review, various aspects of the LBL assembly from technique properties, preparation parameters to possibilities of practical applications have been described comprehensively. Basically, the LBL method is simple, versatile, and flexible in its implementation, which permits various uses based on the requirements of research projects or practical applications [54]. From the various features of the development of LBL assembly, we would like to point out one unique aspect as a potential direction for this research area that is the combination of the LBL technique with CP membrane. CP membranes provide a highly promising platform for the development of an efficient and sustainable technique for separation. However, to achieve separation membranes with a high flux combined with a high selectivity, an ultra-thin defect-free separation membrane is required on top of a highly permeable and mechanically robust support. Thus, LBL methods seems to be ideally suited to provide accurate control over the film thickness on a nanometre-scale and are also free of defects that may be detrimental for separation efficiency [15].

Table 4. Polyelectrolyte multilayers characterization with different techniques and their applications.

Method	Applications	Polyelectrolyte	Substrates	Thickness	P, F	S, SF, R	Ref.
Static assembly	Removal of MgSO ₄	(PDADMAC/PSS) ₅	PES	T - 321	F - 2.47	S - 2.97	[37]
Dip-LBL	Water/alcohol separation	(PVM/PVS) ₆₀	PAN/PET	T - 60	F - 0.5	R - 4% MgSO ₄ SF - 700	[51]
Static assembly	CO ₂ /N ₂ separation	(P4VP/PSS) ₆₀	PAN/PET	T - 60	P - 0.8	S - 1.5	[23]
Dip-LBL	Water/ethanol separation	(PEI/PSS) ₆₀	PAN/PET	T - 60	F - 0.74	S - 12	[23]
Static assembly	Removal of MgCl ₂	(PAH/PSS) ₃	PAN	T - 55	P - 9.8 F - 100	S - 20.9 R - 91.2 % MgCl ₂	[52]
Dip-LBL	Water/isopropanol separation	(PEI/PAA) ₄	PA/PS	-	F - 4.05	SF - 1,075	[53]
Static assembly	Removal of Na ₂ SO ₄	(PDADMAC/PSS) ₄	PS	T - 18.1	P - 60	R - 90% SO ₄	[40]
Dip-LBL	Ethylene glycol/water separation	(PEI/PAA) ₃	PA	-	F - 0.085	SF - 140	[19]
Static assembly	Separation of oligosaccharides	(PAH/PSS) ₅	PAN	T - 24	F - 0.4	S - 46 SF - 340 R - 100% oligosaccharide	[26]
Dynamic assembly Dead-end cell	Water/ethylene glycol separation	(PEI/PAA) ₃	PA	-	F - 0.4	SF - 340	[29]
Dynamic assembly Bottle mouth	Water purification	(PDDA/PSS) ₁₅	PET	T - 190	P - 50	R - 78% methylene blue	[27]
Dynamic assembly Dead-end cell	Water purification	(PDDA/PSS) ₁₅	PET	T - 190	P - 48	R - 98% congo red	[27]
Dynamic assembly Dead-end cell	Water purification	(PDDA/PSS) ₁₅	PET	T - 190	P - 60	R - 70% methyl red	[27]
Dynamic assembly Dead-end cell	Water/alcohol separation	(PEI/PAA) _{2,5}	PAN	-	F - 0.314	SF - 604	[28]
Dynamic assembly Dead-end cell	Water/alcohol separation	(PEI/PAA) _{2,5}	PAN	-	F - 0.338	SF - 833	[28]
Dynamic-static assembly	Water purification	(PAH/PSS) ₃	PAN	T - 34.3	P - 4.96	SF - 400.2 R - 17.78% NaCl	[34]

*Note: Thickness, T - nm; Permeance, P - L/m²h.bar; Flux, F - kg/m²h; Selectivity, S; Separation factor, SF; Retention, R - %; where SF is A/B = (y_A/y_B)/(x_A/x_B) where y_A and y_B are the concentrations of the components A and B in the permeate and x_A and x_B are the concentrations of the components in the feed.

During the last few decades, the application of membrane-based separation is the leading technology as one of the alternatives used in the separating and removal of organic solvents. Moreover, it holds a significant commercial impact in several areas including water and wastewater treatment, chemical, food industries, pharmaceuticals, petrochemical related industries and bio-separation areas [1]. On the other hand, membranes nowadays have fixed physico-chemical properties which make separation by membranes very limited to the fixed selectivity of their constituents [55]. Therefore, new membrane materials must be explored to cope with these limiting factors. The next generation of filtration membranes must be more selective and robust which requires low chemical and energy input [1, 55]. These properties must be considered to meet the goals in applications since current membranes are often problematic in costs. Based on past research, membrane porosity has also been confirmed to be the key factor during the rejection of solutes [37]. LBL techniques are suitable to improve the CP membranes in terms of their morphology, chemical and physical properties, and their performances. The adsorption of neutrally, positively and negatively charged polyelectrolytes onto a CP membrane can contribute to the formation of very thin films and at the same time, able to change the properties of the membrane.

There has been an astonishing amount of progress and development of CP membrane due to the improvisation and fabrication of new membranes. The developments of CP membrane with LBL techniques are quite rapid and surprisingly, there were even some research which proved that LBL and CP membranes with tunable properties can have add-on values in the future, especially for water treatments [26, 28, 51]. However, data reports are particularly scarce in literature. Therefore, a lot more research at the fundamental level are needed as well as used in practical situations. This should attract special attention from the scientific communities and the membrane industries. New contributions to this technique are required for the betterment of membrane technologies.

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