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Reverse Osmosis Desalination Membrane Formed From Weak Polyelectrolytes by Spin Assisted Layer By Layer Technique

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Abstract

Thin film bi-polar membranes were prepared by depositing alternate layers of polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) by Spin Assisted Layer-by-Layer (SA-LbL) coating technique. These polyionic coatings were deposited on silicon wafer substrates as well as on polysulfone ultrafiltration (UF) membranes. The suitability of these coated membranes for use as reverse osmosis seawater desalination membranes was investigated using a single pass cross flow permeation test cell. Membrane testing showed that with only 35 bi-layers of PAH/PAA on a polysulfone ultrafiltration membranes, NaCl rejection of 88% and water permeability of 0.22 L.m⁻²h⁻¹bar⁻¹ was achieved for feed water with NaCl concentration of 15000 ppm and pressure of 700 psig.

Key Words: Reverse Osmosis Membranes, Spin Assisted Layer-by-Layer, PAA/PAH

1. Introduction

Reverse osmosis has been considered as one of the well established technologies in desalination. However, commercial thin film composite (TFC) membranes, which are typically made of polyamide (PA) through interfacial polymerization (IP), still face some major problems in terms of fabrication and performance. Typical commercial PA membrane is usually prepared from two highly reactive monomers e.g. methyl phenylene diamine (MPD) and trimesoyl chloride (TMC). These two monomers dissolve in different solvents, for instance, MPD dissolves in water while TMC dissolves in organic solvents such as hexane. For a thin film to build up, amine must continually cross water-solvent interface, diffuse through already formed polyamide layer. This process may discontinue when amine is no longer able to diffuse through the already build up PA layer. With such formation mechanism, it is difficult to control the thickness and uniformity of the thin film. Some PA membranes even have relatively hydrophobic rough surface which increases susceptibility to biological and particulate fouling.

In this work, we introduced spin assisted layer by layer technique in order to overcome some drawbacks with commercial PA membrane. Layer by layer (LbL) assembly which was introduced by Decher et al [1, 2] is now regarded as one of the most dynamic nanofabrication techniques in the field of thin film technology. It is a rich, versatile, and significantly inexpensive approach to the formation of thin films via alternating adsorption of positively and negatively charged species from aqueous solutions. Nowadays, this technique is even extended to include the alternation of polymers with hydrogen bond as well as donor and
acceptor groups. This technique can also be used to fabricate polymer organic and organic/inorganic thin films that may contain a number of different functional groups [3]. The application of this technique in membrane based separation processes has just recently been investigated. Various types of membrane separation processes such as pervaporation [4-7] and nanofiltration [8-21] have extensively been studied by using the technique over the past decade while quite few works have been done in reverse osmosis [10, 21-24].

We are currently working on fabrication of reverse osmosis membrane by employing two most well studied polyelectrolytes i.e. poly (allyl amine hydrochloride) (PAH) and poly (acrylic acid) (PAA) [25-28]. Spin assisted layer by layer assembly (SA-LbL) was employed instead of dip layer by layer assembly. We showed hydrophilic smooth film was successfully fabricated by such technique. SA-LbL also produces highly internally ordered film within few seconds which also leads to much less interpenetrated layers [29, 30]. This might be thought as another advantage since the film resembles ideal bipolar membrane [9], a characteristic that is difficult to obtain by conventional dip LbL technique.

2. Materials and Methods

2.1. Materials

Poly (acrylic acid) (PAA) with molecular weight of 100,000 g/mol and Poly (allyl amine hydrochloride) (PAH) with molecular weight of 56,000 g/mol were obtained from Sigma-Aldrich. All polyelectrolytes were used without further purification. Polyelectrolyte solutions at prescribed concentration (based on the repeating unit molecular weight) were prepared from 18 MΩ Millipore water (DI water) and pH was adjusted with either HCl or NaOH. N-type, P-Doped [100] silicon wafers with thickness 625 µm were purchased from University Wafer and used as substrate for few base-line studies in this work. Polysulfone UF membrane (YMERSP3001) were purchased from sterlitech and used as substrates for fabricating reverse osmosis membrane.

2.2. Spin Assisted LbL procedure.

SA-LbL deposition technique involves sequential deposition of dilute polyelectrolyte solutions with drying and rinsing between each deposition step. Silicon wafer was cleaned by using 2% v/v Micro-90 solution (NSF) in sonicator bath and followed by thorough rinsing. Prior to deposition, silicon wafers were further treated by air plasma cleaner for 2 minutes. After plasma cleaning, silicon wafers became hydrophilic and negatively charged. Polycationic PAH was thus deposited first onto silicon wafer for 5 sec at a rate of 0.1 mL/sec. Deposition was made exactly when the speed reached the desired spin speed to eliminate the effect of ramp speed during the deposition[31]. Subsequently, the silicon wafer was spin-dried for 20 sec, rinsed for 10 sec with pH adjusted DI water at a rate of 0.2 mL/sec and dried once again for 30s. PAA was deposited on the PAH layer following the similar coat-dry-rinse-dry cycle. Complete cycle (PAH-PAA) was repeated until deposition of specified number of bilayers was achieved. Spin coater used in this experiment was spin coater Model P6700 series (Specialty Coating Systems Inc.). Silicon wafer support was initially used as a base line in order to study the film characteristics and to find optimum condition for coating before we coat polysulfone UF membrane with the same polyelectrolytes.

Another substrate in this study i.e. polysulfone was treated only by using air plasma cleaner for 40 seconds. Polysulfone became somewhat more hydrophilic and negatively charge after this pre-treatment. PAH was firstly deposited for 10 sec at at a rate of 0.2 mL/sec. Coated Polysulfone was subsequently dried for 20 sec; followed by rinsing for 20 sec with pH adjusted DI water at a rate of 0.2 mL/sec. Similar step was also done for PAA and complete cycle (PAH-PAA) was repeated until prescribed number of layer achieved.
2.3. Membrane Characterization

2.3.1. Ellipsometer

The measurement of film thickness on silicon wafers was performed by using Gaertner Scientific 3-Wavelength Variable Angle Ellipsometer operating at a wavelength of 633 nm with incident angle of 70° at ambient temperature. Refractive index of 1.49 was used through all measurements. When studying the growth behavior, measurement was performed from the first layer deposited up on the silicon wafer. The growth then was observed by measuring total thickness after depositing subsequent polyelectrolyte on previously adsorbed layer. This measurement was repeated until prescribed number of layers achieved. The values that are reported in this paper are average of measurements from at least 5 different spots. The measurements for average incremental thicknesses (either bilayer thickness or monolayer thickness) were taken after deposition of 12 layers. Thickness measurement was always done immediately after layer deposition and it was followed by subsequent layer deposition and so on. Therefore the thickness data provided in this work are basically the thickness of relatively wet film since the spin process only remove excess water at the surface film.

2.3.2. Atomic Force Microscope

Contact mode PicoSPM LE from agilent was used to study the surface morphology of the SA-LbL films on polysulfone UF membrane. AFM scanning probes with spring constant of 0.02-0.77 N/m was employed during the characterization. Surface roughness and morphology was taken for sample size of 1 μm by 1 μm.

2.4. Permeation test.

Permeation test was performed by using a cross flow permeation cell CF042 (sterlitech Corp., USA) with active area of 42 cm². Saline water consisting of 15000 ppm of sodium chloride was treated by using SA-LbL RO membrane. The membrane was exposed to deionised water for at least 1 hour for conditioning before use for desalting saline water. Pressure of 700 psig and temperature of 20°C were applied and maintained through entire test. Permeate was collected up to 50 ml and salt concentration of feed and permeate was measured by using a conductivity meter.

3. Results and Discussion

The PAH/PAA bilayer film thickness is strongly affected by pH assembly as shown in Figure 1. Bi-layer assembly at low pH of PAH leads to formation of relatively thin film, while similar trend is observed at high pH of PAA. Therefore, the thinnest film is formed if low pH of PAH is coupled with high pH of PAA. In contrast, the thickest film is formed if high pH of PAH is coupled with low pH of PAA.
This phenomenon occurs because polyacid (PAA) and polybase (PAH) are weak polyelectrolytes whose degree of ionization is strongly influenced by pH. In general, the charges of previously adsorbed layer have to be neutralized with charges of the new adsorbed layer. Therefore, the more the polyelectrolytes get ionized, the higher the charge density is. This means that less polyelectrolyte are required to neutralize previously adsorbed layer. As a result, the thinner films are formed. However, charge density is not the only contributor to the film thickness. For instance, the polymer chain conformation of the previously adsorbed layer and the contour of the underlying surface are also significant in determining the film thickness.

Ideally to achieve high salt rejection, high number of layers is needed because with high number of layers, higher donnan potential is generated, which favours higher ion rejection. However the high number of layers increases film thickness which is unfavourable for achieving high permeate flux. Therefore, in order to obtain high salt rejection but still maintain reasonable water flux, the film has to be as thin as possible. In our case, we selected pH 3.5 for both polyelectrolytes and employed it through all experiments.
Concentration is another important parameter in LbL deposition. Its effect on SA-LbL film can be seen in Figure 2 where film thickness is noted to increase as concentration increases. This result is attributed to the concentration dependent adsorption rate. It is generally known that higher concentration results in higher adsorption rate; consequently higher amount of polymers would be adsorbed at a given time. In LbL case, increasing polyelectrolyte concentration will basically increase the tendency of adsorption of weakly bound polyelectrolytes. Therefore, application of high concentration of polyelectrolyte solution should always be coupled with excess rinsing in order to remove weakly bound polyelectrolytes.

Spin speed is also a significant parameter that is not available in conventional dip LbL assembly. Controlling the spin speed is basically regulating centrifugal force applied during the deposition. As shown in Figure 3, the higher the spin speed the thinner the film because higher centrifugal force applied during deposition can remove not only weakly bonded polymer chains but also to some extent stretch the polymer chains. This result is also confirmed by surface roughness measurement (not shown in this paper) where the RMS roughness decreases from 4.5 nm to 3.3 nm when the spin speed increases from 2000 rpm to 5000 rpm.

Based on optimum condition determined from the baseline study SA-LbL film on polysulfone substrate was fabricated at pH assembly of 3.5, spin speed of 3,000 rpm and polymer concentration of 10 mmol. Because polysulfone is slightly more hydrophobic and rougher compared to silicon wafer, we then injected four times higher volume of polyelectrolyte solution compared to that on silicon wafer to ensure that the polyelectrolytes can completely cover polysulfone surface. After prescribed number of layers is achieved, the as-fabricated-membranes were tested in cross-flow permeation cell to determine their performance.
As shown in Figure 4, increasing number of layers will reduce the water flux because of higher barrier properties, and increase the salt rejection. We reached 75% rejection with only 15 bilayers and 88% rejection with 35 bilayers. Membranes with 35 bilayers show a 40% reduction in permeability but only a 12% increase in rejection. Figure 4 also shows that membranes with 15 and 25 bilayers generate a different flux but yield almost the same rejection. This result suggests that the coating may not completely covers polysulfone. Furthermore, this result also indicates that the water flux is significantly impacted by the film thickness, and implies that optimal coatings would be relatively thin with high degrees of ion rejection.

This result is basically in accordance with theoretical model developed for bipolar membrane. In such membrane, donnan exclusion drives the rejection mechanism more than sieving or steric hindrance effect. Increasing number of layer results in higher donnan potential which obviously provides higher electrostatic repulsive force towards the ions. The stronger the repulsive force the higher the rejection. However, higher number of layers also increases the thickness and tortuosity of the film which in turn decrease water flux.

It was also noticed that the film morphology changed significantly during permeation test. Salt induced morphological or structural change of similar film has actually been studied [32]. In that study, the films were prepared from salt containing polyelectrolyte solutions and then were rinsed with pure water. The film architectures with respect to morphological change were found to be stable if salt concentration in both the polyelectrolyte solution and rinsing solutions were kept constant. This result implies that the film morphology will also remain stable if the films are exposed to salt solution with the same concentration as that of polyelectrolyte concentration.
Figure 5. Morphological change of the film before (a) and after (b) exposing it to solution with high salt concentration (Membranes was polysulfone coated with 15 bilayers of PAH/PAA film, prepared at PAH/PAA pH assembly of 3.5/3.5, concentration of 10 mM, and spin speed of 3000 rpm).

In our case, the condition is the other way around; films were prepared from free salt polyelectrolyte solution and then were exposed to salt solution. Thus, morphological change occurred as expected from the theory. Figure 5(a) showed featureless surface and some of coiled features emerged as shown in Figure 5(b). Applying high pressure during membrane testing basically made the morphological change even more pronounce as the salts are able to further diffuse inside the film and alter the conformation of polymer chains, for instance, the chain can change from stretched to coiled conformation. Hence, the conformation changed not only on the outermost layer but also on the underlying layers.

4. Conclusions

Our study has shown that LbL films are able to reject monovalent ions under reverse osmosis conditions in which 88 % salt rejection was achieved only by depositing 35 bilayers of PAH/PAA on polysulfone. This result was obtained by testing the membrane at pressure of 700 psi and salt concentration of 15000 ppm and we showed that the membrane was comparable to those used in commercial membrane modules that utilize multiple separations, while our membrane was used only in a single pass cross flow permeation cell.

Our study also showed that non-uniformities in the film persist up to several bilayer pairs, which are mainly caused by the surface properties of the membrane substrates used in this study. Simply applying optimum conditions obtained from silicon wafer substrates to polysulfone substrates does not result in uniform films; more optimization works need to be done for integration of these films on polysulfone substrates. However, this preliminary study demonstrates that the technique as well as the materials is quite promising.

It is demonstrated that the SA-LbL technique is a powerful tool to fabricate reverse osmosis membrane. We have shown a simple method to control the film thickness by changing the pH, varying number of layer or altering the spin speed. In the future, different polyelectrolyte combinations will be tested, and several parameters such as pH and spin speed will be further optimized in order to get uniform films, and different numbers of layers will also be deposited to study the effects of film thickness on salt rejection and water flux. In addition to this, the film stability has to be enhanced particularly if the membrane will be used under salt solution.

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