



Micro-morphology and formation of layer-by-layer membranes and their performance in osmotically driven processes



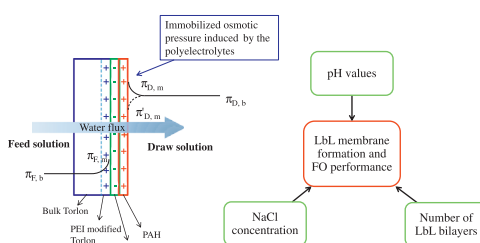
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HIGHLIGHTS

- LbL membranes were fabricated for the forward osmosis process.
- PAS analyses characterize the micro-morphology of the LbL membranes.
- The immobilization of osmotic pressure induced by the LbL membranes is inspected.
- pH values of polyelectrolytes play key roles in membrane formation and performance.
- NaCl in polyelectrolytes induces defects and affects the performance of the membranes.

GRAPHICAL ABSTRACT



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ABSTRACT

We have fabricated novel multilayer membranes for forward osmosis (FO) processes by layer-by-layer (LbL) assembly of polyelectrolytes and examined the fundamentals of LbL membrane formation and microstructure. The LbL membrane was made of a positively charged poly(allylamine hydrochloride) (PAH) and a negatively charged blend of poly(acrylic acid) (PAA) and poly(sodium 4-styrene sulfonate) (PSS) at a weight ratio of 1:1 on top of hyperbranched polyethyleneimine (PEI) modified Torlon substrates and then crosslinked by glutaraldehyde (GA). The newly developed 3-bilayer membrane has an impressive water flux of 28 LMH ($\text{L m}^{-2} \text{h}^{-1}$) and reverse salt flux of 1.97 gMH ($\text{g m}^{-2} \text{h}^{-1}$) using 0.5 M MgCl_2 as the draw solution. Positron annihilation spectroscopy (PAS) analyses reveal that PEI densified the upper layer of the substrate while GA crosslinked the selective layer as well as part of the PEI modified substrate. PAS experiments also indicated that growth in membrane thickness was non-linear and became insignificant after around 6-bilayer of deposition. An immobilized osmotic pressure was observed due to the ion adsorption on the LbL layer. FO results show that the pH and salt concentration of polyelectrolytes play important roles on membrane morphology and FO performance. Both water flux and reverse salt flux were strongly influenced by polyelectrolytes' charge density and the degree of chain coils. Due to strong charge density and chain packing when pH values of PAH and PAA-PSS are 5 and 3–5, respectively, the resultant LbL membranes show both low water flux and low reverse salt flux. The addition of NaCl in polyelectrolyte solutions may facilitate chain coils, rearrange coil size, affect chain packing and create defects depending on NaCl concentration. A relatively high NaCl concentration tends to decompose the coils and weaken the LbL structure, thus increase the water flux but reduce the reverse salt flux.

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1. Introduction

Due to the global concerns on water scarcity and energy depletion, the technologies to produce clean water and renewable

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energy have received worldwide attention (Chung et al., 2012a; Crow, 2012; Escobar and Van der Bruggen, 2011). Forward osmosis (FO) is an emerging technology for water reuse and seawater desalination because there is no hydraulic pressure applied during the water transport across the semi-permeable membrane from the feed to the draw solution (Cath et al., 2006; Chung et al., 2012a, 2012b; Zhao et al., 2012). If suitable draw solutes are available, forward osmosis (FO) might require relatively less energy to produce water from wastewater or seawater in comparison with conventional pressure-driven membrane processes such as nanofiltration (NF) and reverse osmosis (RO). In addition, osmotic energy can be harvested by taking advantages of the salinity gradient across the FO membrane between seawater (preferred RO retentate) and river water under the pressure retarded osmosis (PRO) (Chung et al., 2012a, 2012b; Gerstandt et al., 2008; Skilhagen et al., 2008). If the osmotic power generator and RO plants can be integrated, the overall energy cost for water reuse and seawater desalination may be significantly reduced (Chung et al., 2012a, 2012b). Furthermore, since FO displays smaller fouling propensity than pressure-driven membrane processes (Hausman et al., 2010; Mi and Elimelech, 2008, 2010), FO has also been explored in membrane bioreactors (Achilli et al., 2009; Cornelissen et al., 2008), food concentration (Sant'Anna et al., 2012; Torreggiani and Bertolo, 2004), pharmaceutical processes (Jin et al., 2012; Ling and Chung, 2011; Wang et al., 2011) and direct fertigation (Phuntsho et al., 2011). As a result, the demand to fabricate high performance FO membranes has drawn significant attention for applications in clean water, clean energy and life science.

Basically, the FO membrane is the heart of aforementioned osmotic driven processes, while the driving force in these processes is the osmotic pressure difference across the semi-permeable membrane. Since the semi-permeable membrane allows water to pass through, while rejects salt ions, the desired FO membrane must have this unique semi-permeable property. In terms of industrial practicality, the FO membranes for water reuse and seawater desalination should possess the following characteristics: (i) high water flux and high salt retention; (ii) good mechanical strength and resistance to chlorine, and (iii) low concentration polarization (Cath et al., 2006; Chung et al., 2012a, 2012b; Zhao et al., 2012; Decher, 1997; Su et al., 2012). So far, the lack of effective membranes and draw solutes are the major hurdles for FO processes. Since the layer-by-layer (LbL) assembly of nanometer-thick polycations and polyanions appears to have some semi-permeable characteristics, it brings our attention.

The LbL assembly was first proposed by Decher (1997). Principally, LbL membranes are fabricated by the alternating exposure of the substrate to positively and negatively charged polyelectrolytes. The growth of nanometer-thick polycation/polyanion layers is achieved with electrostatic interaction. Post-treatments such as chemical or ultraviolet (UV) crosslinking can further enhance membranes' pH stability, solvent resistance and long-term stability (Qiu et al., 2011). Since it is a simple method to fabricate ultrathin films with high thermal stability, tunable surface morphology and precise membrane thickness (Dubas and Schlenoff, 1999; Schlenoff and Dubas, 2001), the LbL technology has received attention from many fields such as drug delivery (Endo et al., 2011; Sato et al., 2011), biosensing (Zhang et al., 2007), pervaporation (Ahmadiannamini et al., 2012; Jin et al., 2010; Sae-Khow and Mitra, 2010), NF (Hong et al., 2006), FO (Qiu et al., 2011), fuel cell (Sakamoto et al., 2012) and anti-fouling surface modification (Kuo et al., 2011).

Up to the present, there is very limited research on LbL membranes for FO applications. LbL membranes made of poly(sodium 4-styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) have been fabricated (Qiu et al., 2011; Duong et al., 2013;

Liu et al.; Saren et al., 2011), while only polyacrylonitrile (PAN) and polyethersulfone (PES) have been employed as substrates. The FO performance as functions of (1) membrane formation conditions such as the number of layers and crosslinking reactions and (2) testing conditions such as layer orientation and draw solution concentration have been explored using deionized (DI) water as the feed solution and $MgCl_2$ or NaCl as the draw solute. These early works have demonstrated the potential of using LbL membranes for FO applications. However, the fundamentals and intrinsic properties of LbL membranes have not been fully understood yet. Besides, it is unclear how the fabrication conditions such as pH and salt concentration of polyelectrolytes and substrate properties will influence FO performance.

Therefore, in addition to molecularly design LbL membranes with superior FO performance, we aim to investigate the above issues as well as to study the effects of PEI modification, crosslinking of the LbL selective layer, and the multilayer configuration on FO performance with advanced analytic characterization tools such as positron annihilation spectroscopy (PAS). The new LbL FO membrane will be built on top of the PEI modified Torlon substrate. Since pH and salt (NaCl) concentration are two vital factors that affect the polyelectrolyte conformations, their influence on membrane formation, FO performance and surface morphology will be examined. Moreover, the immobilized osmotic pressure and its influence on membrane performance will be explored.

2. Experimental

2.1. Materials

The Torlon[®] 4000TMW polyamide-imide was purchased from Solvay Advanced Polymers. PEI ($M_w=60,000$ g/mol) (Acro, USA) was used to modify the substrate. The solvent *N*-methyl-2-pyrrolidinone (NMP, > 99.5%), the non-solvent polyethylene glycol 400 (PEG, $M_w=400$ g/mol) were purchased from Merck. NaCl and $MgCl_2$ (Merck, Germany) were used to determine membrane properties. Poly(allylamine hydrochloride) (PAH, $M_w=15,000$ g/mol), 18% poly(sodium 4-styrene sulfonate) (PSS, $M_w=75,000$ g/mol) aqueous solution and 35% poly(acrylic acid) (PAA, $M_w=100,000$ g/mol) aqueous solutions from Sigma-Aldrich were utilized for membrane fabrication. A 50% glutaraldehyde aqueous solution from Sigma-Aldrich was used for membrane crosslinking. (Their structures are shown in Fig. 1.) Pieces of Grade V1 Mica, used for atomic force microscopy (AFM), were purchased from SPI supplies. The deionized (DI) and ultrapure water were produced by a Milli-Q ultrapure water system (Millipore, USA). All chemicals were used as received.

2.2. Torlon substrate fabrication and modification

The Torlon[®] 4000TMW polymer was dried overnight at 80 °C in vacuum oven to remove moisture prior to preparing the dope solution. Dried Torlon[®] 4000TMW (20 wt%) and PEG 400 (30 wt%) were dissolved in NMP at 70 °C overnight. After Torlon[®] 4000TMW and PEG were completely dissolved, ultrapure water (1 wt%) was added to the solution. Subsequently, the polymer solution was left to cool down to room temperature before usage.

The dope solution was cast on a flat glass plate, followed by immersing in tap water to allow for phase inversion to form an asymmetric membrane. After the formation, the membrane was peeled off from the glass plate directly and these membranes were immersed in tap water overnight to remove the residual NMP and PEG.

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