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# Effect of polycation structure on the fabrication of polyelectrolyte multilayer hollow fiber membranes for loose nanofiltration applications



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## ABSTRACT

Polyelectrolyte multilayer (PEM) membranes were fabricated by using a polycation with a long pendant group in order to prepare loose nanofiltration membranes. Poly(2-methacryloxyethyltrimethylammonium bromide)/poly (styrene sulfonate) multilayer membranes were prepared on the lumen side of polyethersulfone hollow fiber membranes with a dynamic coating method and compared to identically prepared poly(diallyldimethylammonium chloride)/poly(styrene sulfonate) multilayer membranes to observe how the different polycation structures affect membrane properties. Both membranes were evaluated in terms of their water permeability, rejection of MgSO<sub>4</sub>, rejection of neutral polyethylene glycol model compounds, and stability against sodium hypochlorite at pH 8.0. Poly(2-methacryloxyethyltrimethylammonium bromide)-based membranes with loose nanofiltration properties and high water permeability were successfully fabricated. However, they degraded rapidly under sodium hypochlorite treatment, whereas the poly(diallyldimethylammonium chloride)-based membranes showed no significant degradation until after 50,000 ppm-h of sodium hypochlorite treatment. Despite the rapid degradation of poly(2-methacryloxyethyltrimethylammonium bromide)-based multilayers under the sodium hypochlorite treatment, the results show that choosing polyelectrolytes with appropriate side group structures can be attractive when designing PEM membranes with membrane properties in the loose nanofiltration range.

#### 1. Introduction

Polyelectrolyte multilayer (PEM) membranes have received much attention in the recent decade for their simple and versatile fabrication method as well as their high permeability and selectivity [1]. The method of fabricating PEM membranes is based on the layer-by-layer deposition of polyelectrolytes [2], via which a multilayer is assembled on a porous substrate by alternately depositing polycations and polyanions. Each polyelectrolyte assembles as a thin nanoscale layer on the substrate, and the resulting multilayer film composed of several alternating layers of oppositely charged polyelectrolytes acts as the selective layer of the membrane, while the porous substrate provides a mechanical support structure for multilayer stability when they are used in membrane filtrations. The layer-by-layer assembly method is highly reproducible and allows for nanoscale control of the multilayer film thickness, and the composition and structure of each individual layer can be varied to affect the properties of the assembled multilayer for particular applications [3]. As such, PEM membranes have a high potential for the fabrication of membranes with tailored membrane composition and separation properties for specific applications.

PEM membranes have been studied for a variety of membrane

filtration applications, such as nanofiltration [4-13], pervaporation [14-18], reverse osmosis [19-22] and forward osmosis [23,24]. The versatility of PEM membrane fabrication has also been exploited to produce anti-fouling membrane surfaces [25,26] and regenerable membranes with sacrificial layers [27-29] to mitigate the performance loss of membranes due to fouling, which is a persistent and inherent performance-limiting phenomenon in membrane separations. The majority of studies conducted on PEM membranes have used the dipcoating method in the deposition of multilavers [2]. Dip-coating involves the immersion of a substrate in an aqueous polyelectrolyte solution and subsequent immersion in a rinsing solution to remove weakly deposited polyelectrolyte molecules, which is then repeated for the oppositely charged polyelectrolyte. Both steps of the sequence are repeated until a sufficient number of layers on the substrate produces the desired membrane properties, the process of which can be time consuming making potential upscaling of the process less attractive. Optimization of the coating process can considerably reduce the time required for multilayer assembly [30]. Alternative coating methods have also been studied to reduce the time required for PEM membrane fabrication so as to make the upscaling of multilayer membrane fabrication more feasible; namely spray-coating and dynamic coating

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[31-37]. Spray-coating replaces the immersion steps of dip-coating with spray technologies, reducing the deposition time of an individual layer significantly [31–33]. The method is, however, unsuitable for the fabrication of PEMs on the lumen side of hollow fiber membranes. In dynamic coating a convective transport of polyelectrolytes to the membrane surface is used to facilitate multilayer fabrication, which has been shown to require significantly fewer deposition steps than PEM membranes fabricated via dip-coating [34-37]. Furthermore, dynamic coating is an attractive method for the fabrication of PEM hollow fiber membranes, since the method can be applied to existing hollow fiber modules. A recent study has also shown that PEM hollow fiber nanofiltration membranes can fabricated to be stable against backwashing and long term oxidative chemical cleaning with hypochlorite, making them attractive as an alternative for polyamide membranes used in processes that utilize oxidative cleaning, although the chemical stability of PEM membranes does depend on the structure of the polyelectrolytes [38].

Despite the extensive research conducted on PEM membranes, only a few studies have focused on the fabrication of PEM membranes with 'loose' structures aimed at the separation of larger organic molecules with molecular weights above 1 kDa [39-40]. Existing studies on the separation of organic molecules with PEM membranes have generally focused on fabricating more 'tight' nanofiltration membranes capable of effectively separating or removing molecules with molecular weights below 1 kDa, such as fractionation of small sugars [11] and removal of micropollutants [13] or dyes [12]. However, membranes with low ion rejection and molecular weight cutoff (MWCO) values in the loose nanofiltration/tight ultrafiltration range (~ 1 kDa or slightly above) can be valuable. For example, the separation of larger dyes can benefit from the generally higher permeability of 'loose' nanofiltration membranes [41-43]. They can also be valuable for drinking water production, in which the removal of natural organic matter from drinking water sources can benefit from nanofiltration membranes that can remove organic matter effectively, but with a low ion rejection to preserve the salt balance of the raw water source [44]. Previous studies on PEM membrane fabrication have shown that such membranes can be approached by varying the coating conditions or the number of deposited layers [10,37,39]. An alternative approach is to fabricate PEM membranes by using polyelectrolytes with appropriate structures.

This study investigates how the structures of two different polycations affect the properties of dynamically assembled PEM membranes, and whether the difference in polyelectrolyte structure can be used to produce a 'loose' nanofiltration membrane. PEM membranes were fabricated on the lumen side of hollow fiber membranes using poly(2methacryloxyethyltrimethylammonium bromide) (PMOTAB) as a polycation and poly(styrene sulfonate) (PSS) as a polyanion. The properties of the PMOTAB/PSS membranes are compared to identically fabricated membranes based on poly(diallyldimethylammonium chloride) (PDADMAC), a commonly used polycation for PEM membranes, and PSS. Both PMOTAB and PDADMAC are quaternary ammonium polymers, and as such strong polyelectrolytes, but PMOTAB has a long pendant group structure. The properties of the membranes are characterized by measuring their permeability to water, rejection of model compounds, and surface charge. The PEM membranes are also subjected to extended sodium hypochlorite treatment and their rejection of a divalent ion is measured to monitor the effect of sodium hypochlorite on membrane performance.

#### 2. Experimental

#### 2.1. Materials

Sulfonated polyethersulfone (PES) hollow fiber membranes (HFS) were obtained from Pentair X-Flow. The hollow fiber membranes had an inner diameter of 0.8 mm and a nominal molecular weight cutoff (MWCO) of 10 kDa reported by the manufacturer. Poly

(diallyldimethylammonium chloride) (PDADMAC,  $M_w = 100-200 \text{ kg/}$ mol) and poly(styrene sulfonate) (PSS,  $M_w = 1000 \text{ kg/mol}$ ) were purchased from Aldrich. Poly(2-methacryloxyethyltrimethylammonium bromide) (PMOTAB,  $M_w = 200 \text{ kg/mol}$ ) was purchased from Polysciences Inc. Sodium chloride (> 99.5%) was purchased from Merck (Ph Eur). Acetic acid (pro analysis) and sodium acetate (> 99%) were purchased from Merck and J.T. Baker respectively. Polyethylene glycols (PEG,  $M_n = 300$  and 1000) and magnesium sulfate (MgSO<sub>4</sub>) heptahydrate (Ph Eur) were purchased from Fluka. Potassium chloride (> 99%) was purchased from Sigma and dried at 450 °C overnight and stored in a desiccator before use. Hydrochloric acid (1.0 M analytical grade) and potassium hydroxide (Titrisol) were purchased from OY FF-Chemicals and Merck respectively and used as received. Sodium hypochlorite (reagent grade) was purchased from Sigma-Aldrich. All water used in the experiments was obtained from an ELGA Labwater Centra-R120 water purification unit equipped with a deionization cartridge ( $\rho > 15 \text{ M}\Omega \cdot \text{cm}$ ).

#### 2.2. Polyelectrolyte multilayer depositions

Polyelectrolyte multilayer depositions were conducted in a custom cross-flow filtration system equipped with separate feed tanks for polycation, polyanion and rinsing solutions. The HFS fibers to be coated with polyelectrolytes were used by potting three fibers inside a lab-scale module, which could facilely be added to and removed from the crossflow filtration system. Before any polyelectrolyte depositions, the HFS membranes were prepared by using a pretreatment protocol recommended by the manufacturer to wet the membrane and remove any residual compounds used in storage. The membranes were thoroughly rinsed with pure water after the pretreatment.

Each polyelectrolyte layer was deposited on the HFS membrane substrate using the following sequence: (1) the polyelectrolyte solution was pumped into the hollow fiber membrane with a cross-flow of 6 L/h per fiber by monitoring the solution conductivity; (2) once the monitored solution conductivity reached the conductivity of the polyelectrolyte feed solution, a 10 min deposition stage was initiated during which the pressure along the whole fiber was kept at 2.0 bar without any cross-flow; (3) after the 10 min deposition stage, the hollow fiber was rinsed with water for 10 min at a cross-flow of 6 L/h per fiber. The polymer concentration of the polyelectrolyte solutions was 1 g/L and polyelectrolytes were dissolved in a 10 mM acetate buffer (pH 5.5) with a NaCl concentration of either 0.2 or 0.8 mol/L. The initial deposited layer was always a polycation, either PDADMAC or PMOTAB, and the sequence described above was repeated by alternating the polyelectrolyte feed solution between a polycation and a polyanion until a desired amount of layers were deposited on the hollow fiber membrane. At least two membrane samples were prepared of each different deposition condition for both polyelectrolyte pairs, and figures showing data with error bars indicate an average value and a deviation obtained from multiple membrane samples. For deposition conditions that showed a high deviation of experimental data, more than two membrane samples were prepared. Experimental data was obtained as described below.

#### 2.3. Filtration experiments

Pure water flux measurements, MgSO<sub>4</sub> filtrations and PEG model compound filtrations were conducted in a custom cross-flow filtration system. Pure water flux measurements were conducted at 25 °C with a transmembrane pressure of 1.5 bar and a cross-flow of 6 L/h (cross-flow velocity  $\approx 3.3$  m/s) per fiber. Pure water filtrations were continued until a steady-state value for pure water flux was obtained. Pure water permeability was calculated from the measured pure water fluxes by normalizing with the transmembrane pressure used in the pure water filtrations. MgSO<sub>4</sub> filtrations were conducted at 25 °C with a transmembrane pressure of 1.5 bar and a cross-flow of 6 L/h per fiber Download English Version:

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