Tailored multi-zoned nylon 6,6 supported thin film composite membranes for pressure retarded osmosis

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HIGHLIGHTS

- Membrane compaction in PRO causes increases in structural parameter.
- Most osmotic membranes are not compaction resistant under PRO conditions.
- A membrane support with an integrated nonwoven scrim is proposed to reduce compaction.
- This support is manufactured on a roll-to-roll casting line at 3M Purification.
- The membrane shows more compaction resistance than a commercial TFC FO membrane.

ARTICLE INFO

ABSTRACT

Sustainable energy can be harnessed from natural or engineered salinity gradients using a process known as pressure-retarded osmosis (PRO). One major challenge is the lack of a suitable semi-permeable membrane that can withstand the pressure of the process yet still employ a support layer that is thin and compaction resistant in order to limit internal concentration polarization. In this study, we report on a roll-to-roll produced thin film composite (TFC) PRO membrane support platform using a thin "multi-zone" nylon 6,6 structure integrated with a nonwoven scrim that enhances mechanical properties and compaction resistance. Two types of TFC membranes with different permselectivities were fabricated based on this support via in-situ interfacial polymerization and then tested under real PRO conditions. Overall our membranes exhibit higher compaction resistance than a commercial FO membrane evidenced by the less severe structural parameter increase under pressure. In addition, our TFC membranes were able to capture 65–81% of theoretical maximum power density performances in comparison to only 50% of the more compactable commercial FO membrane. These results demonstrate that compaction during PRO can substantially reduce power density and the effect can be lessened with appropriate membrane design.

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1. Introduction

Osmotically driven processes are an emerging technology platform that harness the natural phenomenon of osmosis to address water and energy scarcity [1–3]. Osmotic pressure differential can be used to drive the permeation of water for applications of desalination, reuse, and power production. For power production, pressure retarded osmosis can capture the work created when osmotic flow moves against a resistive force. The work from expanding draw solution volume may be captured through a mechanical energy recovery device such as a turbine or pressure exchanger [4–6]. Pioneered by Loeb [4,5,7], PRO is a unique energy harvesting approach that has generated substantial interest over the last decade [6,8–10].

One of the major obstacles to viable PRO technology is the lack of a membrane specifically designed to withstand the typical operating conditions of the process. Of the membrane platforms available, the thin film composite (TFC) has become a popular choice among academic groups and companies. These membranes are fabricated by in-situ interfacial polymerization which forms an aromatic polyamide selective layer on top of a porous supporting structure. This approach has been used to make RO membranes for decades [11–15] and should serve to provide a pressure tolerant and salt selective membrane for PRO. However, as has been determined critical for all osmotic process, the TFC

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support layer must be designed to be thinner, more porous, less tortuous, and hydrophilic in order to reduce the tendency for internal concentration polarization (ICP) [16–19].

Unfortunately, thin, highly porous support layers make for pressure intolerant TFC membranes. Recent studies show that although currently available FO membranes are able to achieve desirable performance in no-or low-pressure FO processes [20,21], they are far from ideal under PRO conditions. The qualities that make the membranes good for FO (thin and porous support layers) have poor mechanical properties under pressure. These membranes can be deformed or even break under typical operating pressures of PRO [22,23]. If they manage to maintain their integrity, the highly porous supporting layers can compact under the pressure, leading to substantial increases in mass transfer resistance and severe ICP. Overall, compaction leads to a substantially lower power density than those predicted by conventional modeling. Some high performance FO flat sheet membranes exhibit high water flux under zero-transmembrane pressure FO while demonstrating power densities of less than 1 W/m^2 under hydraulic pressure in PRO [22,24].

The challenge for PRO membrane designers is to promote good mass transfer and minimal ICP while maintaining mechanical strength. Recently, Song [25] and Bui [26] have introduced intrinsically low diffusion resistant nanofibers as a TFC PRO membrane support. While the compaction of these PRO membranes has never been studied explicitly, our previous work had found that compaction in nanofibers could be significant in pressures less than 10 psi [27]. Self-supported hollow fibers could be another potential option for PRO [10,28,29]. However, these membranes also are not exceptionally pressure tolerant unless they are made with extremely thick walls (high structural parameter) or small lumen sizes (high pressure drop and poor mass transfer using liquids).

Membranes tailored for PRO must exhibit excellent pressure tolerance and compaction resistance while retaining low structural parameter, low cost, and manufacturability. In our previous work [30], we worked with 3M Purification in Meriden, CT to evaluate a commercial nylon based microfiltration membrane (the LifeASSURE™ BLA Series) as a support for a TFC membrane for FO. This membrane was mechanically robust due to an integrated nonwoven scrim, but was also very thick due to the presence of thick porous layers which were needed for microfiltration applications. These membranes consisted of a supporting zone, which was in contact with the polyamide layer, a buffer zone that includes the embedded scrim, and a pre-filter zone that is normally used to prefilter solutions for larger solids during MF, but for this previous work served no purpose. This was discussed as a drawback for using this type of membrane since it was simply used off-the-shelf and was not in any way tailored for use in FO or other osmotic process.

In this study, we tailor this platform by removing the prefilter zone entirely. The resulting membrane is a 2 zone structure with a supporting zone and a buffer zone with embedded mesh. The supporting zone was kept as thin as possible in order to ensure that the scrim would be embedded through as much of the membrane thickness as possible to create a "truss network" to resist compaction the rest of the support. The resultant membrane was half the thickness of the commercial membrane and exhibited a lower structural parameter without sacrificing strength. More importantly, this new membrane was fabricated on a roll-to-roll manufacturing line in collaboration with 3M Purification. This new support was used to support a polyamide selective layer formed through interfacial polymerization and the resulting TFC membrane was tested under FO and PRO conditions.

2. Materials and methods

2.1. Customized supporting membrane

The nylon 6,6 support is manufactured at 3M Purification Inc. (Meriden CT). The process to form the "two-zone" support structure involves casting two dopes of nylon 6,6 solution onto a continuously supplied scrim using a "slot-die" casting apparatus. The scrim is pressure impregnated (pre-coat) with a nylon 6,6 dope first to reach to a desired penetration, which then allows subsequent coating of the supporting zone dope to form finer pores. This insures that the supporting zone does not intrude into the scrim layer which could lower porosity. The membrane is then formed by phase inversion and quenching, which is then rinsed and washed to form the multi-zone membrane. Details of formation methods of this support have been described elsewhere [31].

2.2. Interfacial polymerization

An aromatic polyamide thin film is formed onto the customized supporting membrane via the interfacial polymerization. A 2.0% (wt/v) *m*-phenylenediamine (MPD) solution in water and 0.15% (wt/v) trimesoyl chloride (TMC) in hexane were the reacting solutions. The aqueous phase also contained 2.0% (wt/v) TEA as an acid acceptor. The resulting TFC membrane was denoted as TFC-1. A second TFC membrane with lower selectivity and higher permeance was also prepared for comparison by adding 1.0% (wt/v) DMSO to the MPD solution [32]. This membrane is designated TFC-2.

To make each membrane, the customized nylon 6,6 support was taped onto a glass plate and then immersed into the aqueous MPD solution for 120 s. Excess MPD solution was removed from the support membrane surface using a rubber roller. The support membranes were then dipped into TMC solution for 60 s to form an ultrathin polyamide film. The resulting composite membranes were air dried for 120 s and subsequently cured in an oven at 80 °C for 5 min. The TFC polyamide membranes were thoroughly washed with and stored in DI water at 4 °C before further use.

2.3. Support and TFC membrane characterization

Surface morphology and cross-sectional structure of the TFC membranes were imaged using a cold cathode field emission scanning electron microscope JSM-6335F (JEOL Company, USA). Cross-sectional samples were prepared for cross-sectional imaging using a freeze fracture technique involving liquid nitrogen. A razor blade was emerged into liquid nitrogen with the sample strip simultaneously and then used to quickly cut the sample in half once removed from the liquid nitrogen. Before imaging, samples were kept overnight in a desiccator and then sputter coated with a thin layer of platinum to obtain better contrast and to avoid charge accumulation. The thickness of the TFC membranes was measured using both a digital micrometer at 5 different locations for each membrane sample and cross-sectional SEM images.

2.4. Determination of transport properties in cross-flow reverse osmosis

A bench-scale cross-flow RO testing unit was used to evaluate the pure water permeance, A, and solute permeability, B, of the TFC membranes at 20 ± 1 °C using a method described elsewhere [19,30]. The system was operated at 150 psi with a fixed cross-flow velocity of 0.26 m/s (*Re* ~ 1200) using DI or a 2000 ppm NaCl feed solution to determine A and B, respectively. The determined transport properties were then used to derive structural parameter in FO tests. A commercial sea-water RO membrane (SW30-XLE) was provided by Dow Water and Process Solutions for structure comparison purposes.

2.5. Zero transmembrane pressure osmotic flux tests

Osmotic water flux and reverse salt flux of polyamide TFC membranes were evaluated using a custom lab-scale, cross-flow forward osmosis system described in detail elsewhere. A 0.5 M, 1 M and 1.5 M sodium chloride solution was used as the draw while using DI water as the feed at the temperature of 20 ± 1 °C. Osmotic flux tests were carried out with the membrane oriented in both PRO mode (the membrane