



## Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure

Alberto Tiraferri, Ngai Yin Yip, William A. Phillip, Jessica D. Schiffman, Menachem Elimelech\*

Department of Chemical and Environmental Engineering, Yale University, 9 Hillhouse Avenue, P.O. Box 208286, New Haven, CT 06520-8286, USA

### ARTICLE INFO

#### Article history:

Received 1 October 2010

Received in revised form 2 November 2010

Accepted 7 November 2010

Available online 12 November 2010

#### Keywords:

Forward osmosis

Thin-film composite

Porous support

Polysulfone support layer

Support structure

Support formation

Membrane structure

Internal concentration polarization

### ABSTRACT

Osmotically driven membrane processes have the potential to treat impaired water sources, desalinate sea/brackish waters, and sustainably produce energy. The development of a membrane tailored for these processes is essential to advance the technology to the point that it is commercially viable. Here, a systematic investigation of the influence of thin-film composite membrane support layer structure on forward osmosis performance is conducted. The membranes consist of a selective polyamide active layer formed by interfacial polymerization on top of a polysulfone support layer fabricated by phase separation. By systematically varying the conditions used during the casting of the polysulfone layer, an array of support layers with differing structures was produced. The role that solvent quality, dope polymer concentration, fabric layer wetting, and casting blade gate height play in the support layer structure formation was investigated. Using a 1 M NaCl draw solution and a deionized water feed, water fluxes ranging from 4 to 25 L m<sup>-2</sup> h<sup>-1</sup> with consistently high salt rejection (>95.5%) were produced. The relationship between membrane structure and performance was analyzed. This study confirms the hypothesis that the optimal forward osmosis membrane consists of a mixed-structure support layer, where a thin sponge-like layer sits on top of highly porous macrovoids. Both the active layer transport properties and the support layer structural characteristics need to be optimized in order to fabricate a high performance forward osmosis membrane.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Osmotically driven membrane processes utilize an osmotic pressure difference, which is generated when a semi-permeable membrane separates a dilute feed solution from a more concentrated draw solution, to drive the permeation of water from the feed solution to the draw solution. These processes have the potential to sustainably produce clean drinking water or electric power [1]. Forward osmosis (FO), a subset of osmotically driven membrane processes is appealing because it requires no applied hydraulic pressure and has a low membrane fouling propensity [2]. Because of these benefits, FO is attracting attention as a new technology to augment water supplies using non-traditional sources. The potential of this technology has been demonstrated in a variety of applications, such as desalination [3,4], wastewater reclamation [5–7], industrial wastewater treatment [3,8], brine concentration [9], osmotic membrane bioreactors [10], liquid food processing [3,11,12], and protein concentration [13].

Thus far, one of the major obstacles to the implementation of FO has been the lack of a membrane designed specifically for the process. Such a membrane should reject dissolved solutes, produce high permeate fluxes, be compatible with the selected draw solution, and withstand the mechanical stresses generated during operation. No commercially available membrane currently possesses all of these required characteristics. For example, commercial asymmetric cellulose triacetate membranes are chemically stable only in a small pH window between 4 and 6 [14,15]. The commercial standard for reverse osmosis (RO) desalination of seawater, thin-film composite (TFC) polyamide (PA) membranes, generate low water fluxes when used in FO, as a result of internal concentration polarization (ICP).

ICP occurs because the porous support layer acts as an unstirred diffusive boundary layer. As water permeates across the membrane active layer, the draw solution at the active surface of the membrane is diluted while the diffusion of draw solute from the bulk solution works to restore the concentration at the active layer surface. These competing processes result in a draw solute concentration profile where the concentration at the active layer interface is lower than the bulk concentration, thus reducing the osmotic pressure difference across the active layer [16].

\* Corresponding author. Tel.: +1 203 432 2789; fax: +1 203 432 4387.  
E-mail address: [menachem.elimelech@yale.edu](mailto:menachem.elimelech@yale.edu) (M. Elimelech).

The ideal support layer for FO is very thin, highly porous, and has little tortuosity, thereby providing a short path from the bulk draw solution to the active surface of the membrane (i.e., a thin boundary layer). The dense and thick porous support layer of current commercial TFC RO membranes provides a significant resistance to diffusion, resulting in severe ICP that drastically reduces the water flux. Decreasing the effective thickness of the unstirred boundary layer is essential to minimizing the adverse effects of ICP and to enhancing membrane performance. This characteristic can be achieved by tailoring the structure of the thin-film composite membrane support layer.

During membrane support fabrication by a nonsolvent induced phase separation process, nonsolvent permeates into the film of polymer solution while solvent leaves the film. As a result of this exchange, the composition of the polymer film changes until the stability limit is reached, where the solution phase separates into a polymer-rich and a polymer-poor phase. These two phases eventually form the polymer matrix and pores, respectively [14,17].

Numerous efforts have been made to understand the membrane structure formation mechanism during phase separation. Although theories attempting to quantify or qualify the phenomenon are still being debated, it is accepted that the thermodynamic state and kinetic properties of the system, as well as how they vary during processing, govern the structure formation pathway, and thus, the resulting morphology of a membrane made by phase separation [17–19]. This pathway depends on the temperature, the composition of the casting solution, the composition of the nonsolvent bath, and the surrounding atmosphere. By systematically varying some of these parameters, it is possible to understand how the processing conditions affect the final membrane structure.

Recently, we have demonstrated the fabrication of a TFC membrane tailored for FO operation in a lab-scale setting, exhibiting flux and selectivity performance superior to commercially available FO membranes [17]. This structure was achieved through rational modifications of the membrane casting procedure. The resulting TFC membrane comprises a PA active layer fabricated via interfacial polymerization on top of a porous polysulfone support layer. The modified fabrication procedures allowed the formation of a highly porous support of a finger-like morphology, consisting of macrovoids that span most of the support layer thickness. These macrovoids reduce the resistance to diffusion compared to denser morphologies [17]. In addition, it was proposed that having a thin layer with a sponge-like morphology at the top of the support layer is beneficial to the design of high performance FO membranes [17,18]. The sponge-like layer facilitates the formation of an integral PA active layer, resulting in membranes with higher intrinsic water permeability and improved selectivity [14]. Therefore, the optimal support layer structure reduces ICP without compromising the integrity of the PA active layer [17]. This desired membrane structure was created by using a mixed solvent system and low polymer casting solution concentration during the phase separation step of support layer fabrication [17].

Understanding how membrane structural characteristics influence performance is crucial to further development of membranes designed for FO processes. Here we provide the first systematic investigation on the relationship between membrane support layer structure and FO membrane performance. TFC membranes were fabricated following a two-step procedure: casting of a polysulfone (PSf) support layer onto a polyester (PET) fabric by phase separation followed by the formation of a PA thin film on top of the PSf support layer through interfacial polymerization. Casting parameters for the PSf formation step were systematically varied. Specifically, the roles of solvent composition, dope polymer concentration, substrate fabric wetting, and the gate height of the casting blade were investigated. The resulting TFC membranes were evaluated in RO and FO operations to determine the membrane transport and struc-

|                            |    | DMF Concentration (wt %) → |    |    |    |     |
|----------------------------|----|----------------------------|----|----|----|-----|
|                            |    | 0                          | 25 | 50 | 75 | 100 |
| PSf Concentration (wt %) ↓ | 9  | X                          |    |    |    |     |
|                            | 12 | X                          | X  | X  | X  | X   |
|                            | 15 |                            |    |    |    |     |
|                            | 18 |                            |    |    |    | X   |

**Fig. 1.** Summary of the different recipes employed in the fabrication of the PSf support layers. The columns represent different NMP and DMF mixtures, with the DMF concentration increasing from left to right. Namely, the DMF concentrations are 0, 25, 50, 75, and 100 wt% (based only on the solvent masses) for columns 1 through 5, respectively. The rows represent different PSf concentrations increasing down the column. The PSf concentrations are 9, 12, 15, and 18 wt% for rows 1 through 4, respectively. The investigated recipes are highlighted in grey and crossed. The cell corresponding to 18 wt% PSf concentration in 100% DMF is crossed using a dashed line because the related data is incomplete as explained in the discussion.

tural characteristics. The relationship between these characteristics and the FO membrane performance are evaluated and discussed.

## 2. Materials and methods

### 2.1. Materials and chemicals

Polysulfone (PSf) beads ( $M_n$ : 22,000 Da), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), 1,3-phenylenediamine (MPD, >99%), and 1,3,5-benzenetricarbonyl trichloride (TMC, 98%) were used as received (Sigma–Aldrich, St. Louis, MO). TMC was dispersed in Isopar-G, a proprietary non-polar organic solvent (Univar, Redmond, WA). A commercial polyester non-woven fabric (PET, Grade 3249, Ahlstrom, Helsinki, Finland) was used as a backing layer for the PSf supports. The PET fabric is thinner (40  $\mu\text{m}$ ) and has a more open structure than the typically employed fabric layers [17]. For the membrane performance tests, sodium chloride (NaCl, crystals, ACS reagent) from J.T. Baker (Phillipsburg, NJ) was dissolved in deionized water (DI) obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA).

### 2.2. Polysulfone porous support fabrication

#### 2.2.1. Phase inversion procedure for casting of the polysulfone support layer

PSf was dissolved in the solvent or solvent mixture (Fig. 1) by stirring at room temperature (23 °C) for 8 h and then stored in a desiccator for at least 15 h prior to casting. To begin casting the membrane, the thin, low-density PET fabric was attached to a clean glass plate using laboratory adhesive tape. The PET fabric was then wet with solvent and any excess solvent that pooled on the surface of the fabric was removed using an air knife. The PSf solution was drawn down the PET fabric using a casting knife (Gardco, Pompano Beach, FL) with an adjustable gate height fixed at 250  $\mu\text{m}$  (~10 mils). The whole composite was immediately immersed in a precipitation bath containing 3 wt% solvent in DI at room temperature to initiate the nonsolvent induced phase separation [14,19]. The solvent composition incorporated into the precipitation bath was identical to that used for the preparation of casting dope solution. The same solvent composition was also used for pre-wetting the PET fabric prior to the PSf casting. The support membrane was allowed to sit in the precipitation bath for 10 min, at which point it was transferred to a DI bath for storage until PA formation.

Download English Version:

<https://daneshyari.com/en/article/636047>

Download Persian Version:

<https://daneshyari.com/article/636047>

[Daneshyari.com](https://daneshyari.com)