Influence of macromolecular additive on reinforced flat-sheet thin film composite pressure-retarded osmosis membranes

CrossMark

Jing Wei [a], Ye Li [a,b], Laurentia Setiawan [a], Rong Wang [a,b,*]

[a] Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore 637141, Singapore
[b] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore

ABSTRACT

The salinity gradient is a renewable and sustainable energy source that can be utilized by a pressure-retarded osmosis (PRO) process. Development of the PRO technology was impeded by shortage of efficient membranes until recent surge on PRO research. In this work, flat-sheet thin film composite (TFC) PRO membranes with reinforced support layer were developed. The membrane properties were optimized by blending high molecular weight polyvinylpyrrolidone (PVP) into the polysulfone (PSf) casting solution. Influences of PVP addition on the kinetic and thermodynamic properties of the casting solution, resultant membrane properties as well as PRO performance were systematically investigated. It is showed that PVP can effectively improve the membrane morphology and pore structure. By adjusting the PSf/PVP composition in the substrate recipe, the reinforced TFC membrane is able to achieve a power density of 12.9 W/m² at 22 bar using 1 M NaCl draw solution and pure water feed. Long-term PRO test at the peak power density and multi-pressure cycle tests were performed on the membranes. Consistent power density and low salt flux/water flux ratio were observed in the whole tests. The results demonstrated that the reinforced TFC membrane in this study had excellent mechanical strength and stability. It would be promising for future engineering application.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In line with the accelerating growth of global energy consumption, the exploitation of renewable energy sources continued to increase in the past decades. In 1970s, utilization of salinity gradient power via pressure-retarded osmosis (PRO) was invented by Sidney Loeb [1]. Salinity gradient power (or osmotic power) is a renewable energy generated from the controlled mixing of two liquids with different osmotic pressures. In the PRO process, a high osmotic pressure liquid (e.g., brine) and a low osmotic pressure liquid (e.g., freshwater) are separated by a semi-permeable membrane that allows water permeation but rejects solute. As water permeates from the freshwater side to the brine side, driven by the osmotic pressure difference, a hydraulic pressure lower than the osmotic pressure difference is applied on the draw side to retard the water flux. In the engineering design, the diluted brine could be partly circulated to a pressure exchanger to pressurize the brine influent, while another stream will be depressurized by a hydro turbine to produce electric power [2]. No greenhouse gas will be emitted during the PRO process. Moreover, it is estimated that around 2000 TWh power could be harvested yearly from the

mixing of seawater and river water in the estuaries globally [2]. More salinity gradient energy sources such as the Dead Sea and the Great Salt Lake are investigated as well [3]. Therefore, exploitation of the salinity gradient energy by PRO is a sustainable topic for study.

Although the PRO process has been brought forward for half century, it was only until the last decade that increasing researches on this field were presented [4]. One of the major technical barriers to the development of PRO is the lack of suitable membranes. Most of the commercially available membranes are designed for pressure-driven processes such as reverse osmosis (RO) or nanofiltration (NF). These membranes typically consist of an active rejection layer and a porous support layer. To withstand the hydraulic pressure in NF/RO processes, this support layer has to have a relatively dense pore structure and a compact non-woven fabric at the bottom. In the osmotically-driven membrane process, severe concentration of feed solution (in the active layer facing draw solution (AL-DS) orientation) or dilution of draw solution (in the active layer facing feed solution (AL-FS) orientation) will occur in this type of support layer due to their low mass transfer coefficient [5]. This internal concentration polarization (ICP) phenomenon can drastically reduce the effective osmotic pressure difference, resulting in low water flux and low power density in PRO process. Fabrication of high efficiency membranes is crucial for the practical application of PRO technology.

With the emerging attention to osmotically-driven membrane processes, a number of new membranes have been designed during the last decade for forward osmosis (FO) [6]. It is revealed that high-performance FO membranes should have small structural parameter (S) for lower ICP, a good combination of water permeability (A) and selectivity for high water flux and minimal impact of solute reverse diffusion. The thin film composite (TFC) configuration is very promising as the membrane permeability and selectivity can be tuned by optimizing the polyamide rejection layer, while the S value can be reduced by using a thin and highly porous substrate with finger-like pore structure [5,7]. A critical difference between FO and PRO is the high pressure applied on the draw side of the membrane. The FO membranes would be susceptible to deform and damage in PRO tests. Therefore, a challenge in PRO membrane fabrication is to achieve both high water flux and high mechanical strength.

A few PRO membranes with enhanced performance were reported recently. Hollow fiber membranes have attracted great interest due to their self-supporting structure. Chou and Wang et al. first reported a TFC hollow fiber with polyethersulfone (PES) substrate for PRO process [8]. Another type of TFC hollow fiber with polyetherimide (PEI) substrate was reported afterwards, which exhibited power density of 20.9 W/m^2 using 1 M NaCl draw solution and 1 mM NaCl feed solution [9]. The studies illustrated the different requirement on the support structure of FO and PRO membranes, i.e., a sponge-like support might be preferred over a macrovoid-containing support in PRO. TFC hollow fibers with other polymeric substrates such as polyimide (Matrimid) [10–13], P84 co-polyimide [14], and PES grafted with synthetic hyperbranched polyglycerol for anti-fouling properties [15], etc., as well as various configurations (e.g., dual-layer hollow fiber [16] and TFC hollow fiber with tri-bore substrate [17]) were reported by Chung et al. Industrial application of hollow fiber PRO membranes has been carried out by Toray Industries, Inc. (Japan) as well [18].

Flat-sheet membranes for PRO process have also been studied. This type of membranes can have high mechanical strength when they consist of a reinforcing layer in the support, according to the practice in pressure driven membrane applications. Thus the flat-sheet membranes would be able to generate high power density in PRO process as well. Nevertheless, the development of flat-sheet PRO membrane was relatively slow. Song [19] and Bui [20] presented electrospun nanofiber-supported TFC PRO membranes that consisted of a polyester non-woven fabric at the back of the nanofiber. Besides, Han [21] and Cui [22] reported TFC membranes with macrovoid-free Matrimid substrate. Fu [16] reported dual-layer membranes prepared via co-casting method. However, no reinforcing fabric was incorporated in these membranes. In scale-up PRO process, spacers with large opening would be necessary in both feed and draw sides to support the membrane and mitigate external concentration polarization (ECP) and foulant accumulation. The feed spacer tends to cause severe membrane deformation when high pressure is applied on the draw side [23], which could damage the membranes without reinforcing layer. This is similar to the high pressure RO modules, of which the membranes are typically designed to have a thick and compact non-woven fabric at the back to withstand the high pressure.

TFC flat-sheet PRO membranes with high mechanical strength were developed in this work by incorporating a porous reinforcing fabric. To improve the morphology of the reinforced membrane, a blended polymer system of polysulfone (PSf) and high molecular weight polyvinylpyrrolidone (PVP) was used to prepare the support layer. The kinetic and thermodynamic properties of different PSf/PVP casting solutions as well as their influence on the membrane performance were systematically studied. To further observe the stability of the reinforced TFC membranes, long-term PRO tests and pressure cycle tests were performed to investigate the potential for future engineering application.

2. Experimental

2.1. Chemicals and materials

Polysulfone (PSf, Mw 75,000–81,000 Da, Solvay), polyvinylpyrrolidone (PVP, Mw 1,300,000, Alfa Aesar) and N-methyl-2-pyrrolidone (NMP, Merck) were used to prepare substrates. M-phenylenediamine (MPD, Sigma-Aldrich), sodium dodecyl sulfate (SDS, Scientific Apparatus Supplier), trimesoyl chloride (TMC, Sigma-Aldrich), n-hexane (Merck) were used for synthesizing membrane selective layer. Sodium chloride (NaCl, Merck) was used to evaluate membrane performance. All chemicals were of analytical grade and used as received. Deionized (DI) water with a resistivity of 18.2 MΩ cm was produced by a Milli-Q ultrapure water system (Milli-pore). Polyethylene terephthalate (PET) mesh (Anping SY) was used as reinforcing fabric to prepare the substrates.

2.2. Membrane preparation

The reinforced PSf substrates were prepared by non-solvent induced phase separation. PSf and PVP with varied concentrations were dissolved in NMP by stirring at 70 °C. The homogeneous dopes were cooled down to room temperature (24 ± 1 °C) and degased before use. The compositions of four casting solutions are showed in Table 1. Before casting, a PET mesh was attached on a glass plate using adhesive tape. The dope was spread onto the mesh using a motorized film applicator (Elcometer 4340). A clearance of 200 μm was applied for all membranes. The entire composite and glass plate were immersed into a room temperature water bath to induce phase separation. The solidified substrate separated from the glass plate, and then was transferred to a flowing water bath in order to remove residual solvent. The clean substrates were stored in DI water before use.

A polyamide selective layer was synthesized on the reinforced substrate via interfacial polymerization. The substrate was first soaked in an aqueous solution of 1.5 wt% MPD and 0.1 wt% SDS for 5 min. Compressed nitrogen gas was then used to sweep and remove the water droplets on the surface, following by contacting the membrane surface with an n-hexane solution of TMC (0.15 wt%) for 1 min. The resultant TFC membrane was rinsed in water bath and stored in DI water for characterization.

2.3. Membrane characterization

The rheology of casting solutions was evaluated using a rheometer (Physica MCR101, Anton Paar). During the testing, casting solution was placed on a horizontal plate and the measuring cone was lowered to contact with the dope and formed a thin dope layer in-between. Temperature and relative humidity were maintained at 25 °C and 60 ± 2%, respectively. As the cone rotated, the shear rate applied on the dope was increased from 0.01 S^{-1} to 1000 S^{-1}. The shear stress at varied shear rate was recorded to calculate the viscosity.

The phase diagram of PSf/NMP/water system was determined via cloud point titration. The PSf/NMP solutions with various concentrations (5%, 10%, 15%, 20%, 25% and 30% by weight) were firstly prepared to determine the binodal curve without additive. Another three solutions with PVP were prepared by adding 1%, 3% and 10% PVP into the PSf/NMP solutions, which had the identical

Table 1
Casting solution compositions of reinforced flat-sheet substrates.

	PSf (wt%)	PVP (wt%)	NMP (wt%)	Viscosity at shear rate of 1 s^{-1} (Pa s)
S-0	26	0	74	10.7 ± 1.8
S-1	16	8	76	25.4 ± 0.4
S-2	16	10	74	66.5 ± 5.8
S-3	16	12	72	127 ± 4