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Identification of safe and stable operation conditions for pressure retarded osmosis with high performance hollow fiber membrane

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ABSTRACT

Pressure retarded osmosis (PRO) is a promising energy harvesting technique. However, when polymeric hollow fiber membrane is used for the PRO process, the mechanical strength of the membrane is a big concern. As hollow fiber membrane is self-supported and due to its polymeric nature, it may gradually deform over time under high pressure loading, or membrane "creeping" will occur. Current work is the first attempt to analyze the membrane creeping phenomenon of a novel thin film composite (TFC) hollow fiber. The membrane creeping was evaluated via nanoindentation by using atomic force microscope (AFM). A non-stop 200-hour PRO test and integrity check, which have not been reported previously, were carried out to investigate the membrane performance under various operating pressures. The results show that the membrane is able to produce a stable power density output of 19.2 W/m^2 at 15.0 bar, using 1.0 M NaCl as the draw solution and DI water as the feed water. Membrane creeping was observed when the applied pressure exceeded the safe operation limit (or the flux turning point, where the membrane flux started to increase with increasing applied pressure in the PRO mode), which caused an irreversible damage to the membranes. This study identified safe and optimum operation conditions of the laboratory-made PRO hollow fiber membrane to achieve the most favorable PRO performance. It provides guidance for practical applications of polymeric hollow fiber membranes in PRO process.

1. Introduction

Over the last century, global population grew considerably and the global economy developed rapidly. As a result, the demands for water and energy have been intensified world-wide, which stimulated the exploitation of new energy resources. Osmotic energy, where pressure retarded osmosis (PRO) system could potentially be used to harvest a significant amount of renewable energy from two streams with different salinities, was first proposed by Loeb in 1970s [1]. However, due to limited availability of commercial membranes on the market, few PRO experiments were conducted to improve the technology [2,3]. Recently, the PRO technology gains increasing popularity with advancement in membrane fabrication technology, which potentially offers a renewable solution for the depletion of the world's petroleum reserves.

Based on the osmotic process type, membranes can be classified as reverse osmosis (RO), forward osmosis (FO) or direct osmosis (DO) and pressure retarded osmosis (PRO). RO utilizes hydraulic pressure to overcome the osmotic pressure difference to push freshwater from a high salinity solution to a low salinity solution across a semi-permeable membrane. RO has been extensively studied and utilized for seawater desalination and waste water reclamation [4–6]. FO, on the other hand, is a concentration-driven process where water diffuses naturally from a low salinity solution to a high salinity solution across a semi-permeable membrane. In spite of its inability to produce freshwater directly, FO has attracted much attention recently for several potential applications and hybrid systems [7–10]. PRO is an osmotic energy-recovering process that derives from the natural phenomenon of osmosis. Similar to FO process, water transfers from a low salinity solution at ambient pressure via a selectively permeable membrane to a pressurized high salinity solution. The increased volume of pressurized solution is able to drive a turbine for power generation [11].

Though PRO has been intensively studied recently, many problems need to be addressed. Studies on PRO processes reveal that experimental PRO water flux tends to be significantly lower than the theoretical values due to internal concentration polarization (ICP). The presence of ICP reduces the effective osmotic driving

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force resulting in a lower power density [12]. ICP was first discussed in late 1970s [2], and further developed into a conceptual model by the early 1980s According to the model developed by Lee et al. [3], it is possible to eliminate ICP if the mass transfer resistance is minimized. Subsequently, the ideal support layer for PRO is thought to be as thin and porous as possible [13]. On the other hand, the membrane should possess an excellent mechanical strength to withstand high hydraulic pressures and long term operation. Theoretically, a maximum power density exists when the hydrostatic pressure difference is equal to half of the osmotic pressure difference, suggesting the optimal working condition for a PRO system.

Many attempts have been made to fabricate high performance osmotic-driven membranes both in hollow fiber and flat sheet configurations. Generally, an FO/PRO membrane consists of an RO-like selective layer supported by a permeable layer providing the necessary mechanical support with the least mass transfer resistance. A commercial flat sheet osmotic membrane made of cellulose triacetate (CTA, HTI) embedded on a polyester woven mesh has been used in a PRO process. The membrane is able to withstand a hydraulic pressure of 17 bar and power density of 5.8 W/m^2 can be achieved [14]. A polybenzimidazole (PBI) – polyacrylonitrile (PAN) dual-layer thermally annealed hollow fiber membrane had a peak power density of 5.1 W/m^2 at 15 bar when 1.0 M NaCl and 10 mM NaCl were used as the draw and feed solutions, respectively [15]. Hollow fiber membranes made from polyethersulfone (PES) as the support layer and a thin film composite (TFC) of polyamide as the selective layer was fabricated for FO applications. It was found that the finger-like structure of pores in the support layer is able to greatly mitigate the ICP effect [16]. This method was further improved to fabricate a PRO membrane with a power density of 11 W/m^2 at 9 bar [12]. Moreover, to further enhance the mechanical strength, polyetherimide (PEI) was used as the substrate material and the structure of the hollow fiber membrane was controlled to give a sponge-like morphology. This membrane was able to achieve power density of 20.9 W/m^2 at 15.1 bar operating pressure [17]. Zhang et al. developed thin film composite PES hollow fiber membranes with power density of 24.3 W/m^2 at 20 bar by using 1.0 M NaCl as the concentrated brine and DI-water as the feed water [18].

However, it should be pointed out that while different types of PRO membranes have been developed, the long-term PRO performance of resultant membranes and comprehensive integrity check were not reported in the literature. Investigations on membrane stability tested over long-term operation have been elusive. It is well understood that due to its polymeric nature, polymeric membrane may gradually deform over time under high pressure loading, or membrane “creeping” will occur. The creeping phenomenon would eventually damage the membrane and deteriorate the membrane performance to complete failure.

The current study aims to investigate the stability of an in-house made high performance PRO hollow fiber membrane in order to identify safe and stable operating conditions over long term testing under a high hydraulic pressure. The support layer was made of PEI, providing an excellent mechanical support and low trans-membrane mass-transfer resistance. The selective layer of polyamide was prepared by interfacial polymerization. The PRO hollow fiber membrane was pressurized at various hydraulic pressures in RO and PRO modes in order to understand its performance behavior. After obtaining an entire picture, the membrane was pressurized at specific hydraulic pressures for a long period of time to study the time effect. The PRO hollow fiber membranes were then characterized using various techniques including nanoindentation by using AFM for membrane creeping evaluation. The performance of the PRO hollow fiber membranes was tested on a laboratory scale PRO setup. This study is believed to be the first effort to investigate the creeping phenomenon of PRO hollow fiber membrane due to high pressure loading and to report PRO membrane performance over a long term test of 200 h. It is expected to provide guidance for practical applications of polymeric hollow fiber membranes in PRO process.

2. Experimental methods

2.1. Materials

Polyetherimide (PEI Ultem 1000, GE Plastic, USA) was used to make the porous hollow fiber substrates. N-methyl-2-pyrrolidone (NMP, > 99.5%, CAS#872-50-4, Merck Chemicals, Singapore) was used as the solvent. Polyethylene glycol (PEG, CAS#25322-68-3, Merck Chemicals, Singapore) was used as a pore former for the substrate. Purified water by a Milli-Q system (18 MΩ cm) and tap water were used as the bore fluid and the external coagulant, respectively. Dextrans with different molecular weights (6000–500,000 Da; $(C_6H_{10}O_5)_n$, Sigma Aldrich) were used to determine the molecular weight cut off (MWCO) of the substrate. Glycerol (85%, CAS#56-81-5, Merck Chemicals, Singapore) was used to post-treat the membrane for storage purposes. 1,3,5-Benzenetricarbonyl trichloride (TMC, CAS# 4422-95-1, Sigma-Aldrich) and *m*-phenylenediamine (MPD, CAS# 108-45-2, Sigma-Aldrich) were used as the monomers for the interfacial polymerization. Cyclohexane (CAS# 110-82-7, Merck Chemicals, Singapore) was used as the solvent for TMC. Sodium chloride (NaCl, CAS# 7647-14-5, Merck Chemicals, Singapore) was used to prepare the feed and draw solutions.

2.2. Fabrication of PRO hollow fiber membranes and modules

PEI hollow fiber substrates were fabricated based on the non-solvent induced phase separation (NIPS) method by a dry jet–wet spinning technique. The polymer and the additive were completely dissolved in NMP prior to spinning. The details of the hollow fiber spinning process and post-treatment can be found elsewhere [17,19].

Fifteen pieces of hollow fibers were potted into a tube with effective length of 22 cm and sealed by epoxy. The active–selective layer was subsequently developed on the inner surface of the PEI hollow fiber substrates by interfacial polymerization of TMC and MPD at ambient temperature as described in the literature [9]. The hollow fiber membranes with the selective layer would be known as PRO-PEI HF.

2.3. Characterizations and analysis

The dimension of PEI hollow fiber substrates was measured by a Keyence VHX 500F Digital Microscope. A mean value was obtained based on the measurement of ten different fibers. The structure and morphology of the fiber cross-section and surface were examined by a Jeol JSM-7600F field emission scanning electron microscope (FE-SEM). The wet hollow fiber membranes were dried in a freeze drier overnight prior to be fractured in liquid nitrogen. The samples were subsequently mounted on the SEM stubs followed by platinum sputter coating.

Pure water permeability (PWP) and molecular weight cut off (MWCO) of PEI hollow fiber substrates were tested by using a bench scale cross-flow filtration system at a constant pressure of 1 bar. Ten pieces of hollow fiber substrates were potted into a tube (with effective length of 25 cm) and sealed by epoxy. Distilled water was circulated through the lumen side of the module to get PWP. The MWCO of PEI hollow fiber substrate was determined by