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Preparation, characterization and performance evaluations of thin film composite hollow fiber membrane for energy generation

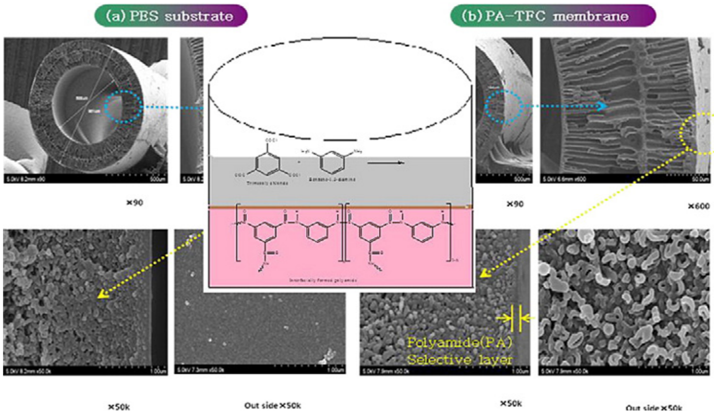
Pravin G. Ingole, Wook Choi, Kee-Hong Kim, Hang-Dae Jo, Won-Kil Choi, Jong-Soo Park, Hyung-Keun Lee *

Greenhouse Gas Research Center, Korea Institute of Energy Research (KIER), 71-2 Jang-dong, Yuseong-gu, Daejeon 305343, Republic of Korea

HIGHLIGHTS

- For the first time the potential of different types of TFC-HFM for PRO is explored.
- Implications of the results for power generation by PRO are evaluated and discussed.
- Effect of MPD, TMC monomer and reaction time on the PRO performance is demonstrated.
- The TFC-HF membranes show enhancements in both water flux and power density.
- An overall comparison and discussion of hollow fiber aspect design are made.

GRAPHICAL ABSTRACT



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ABSTRACT

This article analyzes the different types of thin film composite hollow fiber (TFC-HF) membranes and their performance of pressure retarded osmosis (PRO) for power generation. Pressure retarded osmosis (PRO) is an osmotically-driven membrane process that can be used to harvest salinity-gradient power. For the first time, the potential of using different types of TFC-HF membranes for PRO has been explored. Several types of TFC-HF membranes with well-designed substrate structures were prepared. This study systematically investigates the effects of operating conditions and effect of membrane preparation/fabrication conditions such as concentration of monomers like *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC), effect of reaction times, effect of pressures on the membrane performance using KIER manufactured polyethersulfone (PES) HF membranes as a substrate. The TFC-HF membranes show reasonably high water fluxes under the PRO mode using 0.6 M NaCl as the draw solution and deionized water as the feed solution. Moreover, the surface and skin morphology of the substrate may play an essential role in the formation of the polyamide layer as well as in its perfectness and PRO performance. The implications of the results for power generation by PRO are evaluated and discussed. Our results provide significant implications for PRO scaling control.

1. Introduction

Energy is the essential possession for public health and economic prosperity. PRO is an emerging platform technology that has the potential to sustainably produce electric power. It has therefore garnered great interest amongst the membrane science community within the

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* Corresponding author. Tel.: +82 42 860 3647.
E-mail address: hklee@kier.re.kr (H.-K. Lee).

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last decade [1–3]. To reduce the control on fossil fuels while also satisfying growing energy requirements, new alternative sources have to be explored and embraced, particularly renewable sources due to the smaller impact on our environment. A grand quantity of renewable energy can be potentially generated when waters of different salinities are mixed together. The generated osmotic pressure difference drives the permeation of water across the membrane from the dilute solution to the concentrated solution. The applications include direct osmotic concentration (DOC) for concentrating high-value solutes, forward osmosis (FO) for seawater desalination and PRO for electric power generation [4–8].

With fast economic development and remarkable increase in population, the world is facing distinctive challenges of energy supply. For global sustainable development, there is a need to reduce green house gas (GHG) emissions from fossil fuels which has focused the attention on alternative energy sources such as solar, wind, and geothermal energy, and the solution of these problems is the generation of osmotic power [9]. S. Loeb et al. reported innovative experimental work on PRO in 1976 [10], when a U-shape hollow fiber membrane, originally designed for seawater desalination, was used in a PRO mini-permeator to demonstrate the feasibility of the PRO process for power generation. However, the observed water flux from the feed water to the draw solution was much lower than expected due to the severe concentration polarization that occurred in the thick and dense support layer of the membrane. This so-called internal concentration polarization (ICP) was first discussed/discovered by Mehta and Loeb [11], and subsequently analyzed with a theoretical model developed by Li et al. [12], which has been widely employed recently in FO and PRO related studies. ICP is considered as the most severe constraint in the osmotic membrane processes, as it significantly depresses the water permeation across the membrane [13].

The osmotic power can be subsequently harvested in the form of electricity by running the pressurized draw solution through a hydroturbine generator [14,15]. Recent publications in the form of review articles have been published by some researchers for the comprehensive study of the PRO technology [2,16,17]. The PRO technology, pioneered by Leob [14,18,19] has received significant interests in the past few years [20–25]. While early PRO studies using asymmetric reverse osmosis membranes observed extremely low power density due to their thick support layers [26–29], recent developments in osmotic membranes and processes have shown promising progresses [28–30]. A hydrophilic polymer supported thin film composite membrane, possessing the benefits of PRO membranes, might be suitable for power regeneration processes. It is highly possible that this membrane still retains the high permselectivity as commercial RO membrane, and low resistance to mass transfer like commercial FO membranes due to improved hydrophilicity of the support membranes.

The membrane structure parameter (S parameter) can significantly affect the membrane performance. The PRO process will require a membrane with low structure parameter (S), in addition to high water permeability and low salt permeability. The structure parameter is defined as the ratio between tortuosity and porosity multiplied by the thickness of the membrane, and can be regarded as a measure of the effective diffusion length in the support structure. The S parameter represents the resistance to salt transport in the porous substrate (support layer of the membrane). The S parameter determines the extent of ICP and has to be minimized to produce a higher water flux [31]. RO membranes have a large S value (which means that they are thick and dense), because the membranes have to withstand high applied hydraulic pressures. In PRO, however, the support layer can be much thinner and with larger porous, which would increase the flux of water though the membrane.

In this study the effects of operating conditions i.e. effect of membrane preparation/fabrication conditions such as concentration of monomers, concentrations of TMC, effect of reaction times, effect of pressures on the membrane performance and PRO performance using KIER manufactured PES hollow fiber membranes as a substrate were systematically investigated. The TFC-HF membranes show with reasonably high water fluxes under the pressure retarded osmosis (PRO) mode using 0.6 M NaCl as the draw solution and deionized water as the feed. The phenomenon of reverse solute diffusion and its adverse effect on PRO performance will also be discussed. Results obtained in this study may provide significant insight into the PRO operation and PRO membrane design conditions.

2. Theory

2.1. Standard osmosis processes

The semi-permeable thin film membrane only allows the passage of water but fully rejects other solute molecules/ions, the water flux in an osmosis process can be depicted as

$$Jw - A(\Delta\pi - \Delta P) \tag{1}$$

where Jw is the volumetric water flux through the membrane, A is the water permeability of the membrane, and Δπ and ΔP are the osmotic and hydrostatic pressure differences across the membrane, respectively. PRO is an intermediate osmosis process between the FO and RO, where the hydrostatic pressure of the draw solution is lower than the osmotic pressure difference across the membrane, so that the water permeates from the feed (fresh water) side to the draw (salty water) side. In terms of energy production or consumption, which is normally evaluated based on power density defined as the product of the transmembrane hydrostatic pressure of the draw solution and the water flux permeating across the membrane, the power density (W) versus hydrostatic pressure difference based on Eq. (2) is computed as:

$$W = Jw\Delta P = A(\Delta\pi - \Delta P)\Delta P. \tag{2}$$

It can be seen that pressure energy is produced in the PRO process by transferring the water from a low pressure side to a high pressure side i.e. feed side to draw side. The energy density i.e. the amount of osmotic power produced per membrane area is a major performance indicator in PRO process, as it determines the amount of membrane area and thus the size of the PRO plant for a given energy production capacity. There exists a maximum power density when the hydrostatic pressure difference is equal to the half of the osmotic pressure difference, suggesting the optimal working condition for a PRO system.

3. Experimental

3.1. Materials

Polyethersulfone (PES, Ultrason® E6020P, BASF, Germany), used as the base polymer was purchased from General Electric Company. N-methyl-2-pyrrolidion (NMP) with purity more than 99.5% was purchased from Merck and was used as solvent without further purification. Lithium chloride (LiCl, Sigma Aldrich) was used as pore former in dope solution. Diamine monomer m-phenylenediamine (MPD) and acid chloride monomer trimesoyl chloride (TMC) were purchased from Sigma-Aldrich. Hexane, the solvent for TMC, was purchased from Fisher Scientific. Deionized water (DI) obtained from a Milli-Q ultrapure water purification system (Millipore) was used as the solvent for diamine monomers. Sodium chloride was purchased from Fisher Scientific.

3.2. Methods

3.2.1. Preparation of PES hollow fiber membrane

Hollow fiber membranes were produced by a wet phase inversion method [32]. Commercially available PES was used as membrane