Applied Energy 114 (2014) 600–610

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Thin-film composite P84 co-polyimide hollow fiber membranes for osmotic power generation

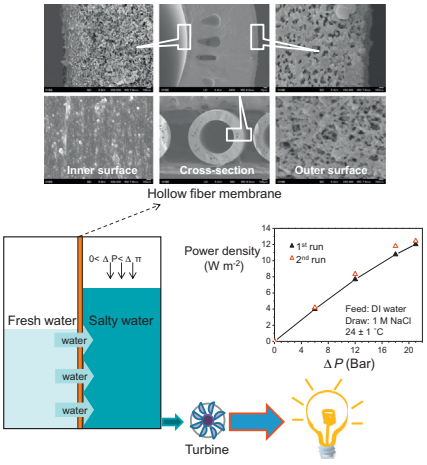
Xue Li [a], Tai-Shung Chung [a,b,*]

[a] NUS Graduate School for Integrative Science and Engineering, National University of Singapore, Singapore 117456, Singapore
[b] Department of Chemical & Biomolecular Engineering, National University of Singapore, Singapore 117576, Singapore

HIGHLIGHTS

- Novel thin-film composite (TFC) hollow fiber membranes are molecularly designed and developed.
- The membrane supports achieve superior tolerance to high pressures up to 23 bar.
- The TFC membranes perform well in pressure retarded osmosis (PRO) process.
- The effect of flow rate on PRO was investigated for the first time.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form 11 October 2013
Accepted 14 October 2013
Available online 6 November 2013

Keywords:
Hollow fibers
Osmotic power generation
Thin-film composite membrane
Pressure retarded osmosis

ABSTRACT

A series of well-designed thin-film composite (TFC) hollow fiber membranes via dual-layer co-extrusion technology for pressure retarded osmosis (PRO) applications is reported in this work. By controlling the phase inversion process during spinning, we have molecularly engineered hollow fiber membranes with various structures, dimensions, pore characteristics, and mechanical properties as supports for the synthesis of TFC membranes. Under hydraulic tests, these hollow fiber membrane supports possess high burst pressures from 13 to 24 bar. The TFC membranes fabricated by interfacial polymerization on the inner surface of the hollow fiber supports not only exhibit relatively high power densities of 5–12 W m^{-2} but also display a superior tolerance to high pressures up to 21 bar. The TFC membrane synthesized on a small dimensional hollow fiber support, which was spun from a P84 co-polyimide/ethylene glycol (EG)/*N*-methyl-2-pyrrolidinone (NMP) dope solution with a bore fluid of a water/EG/NMP mixture, shows the most impressive PRO performance (i.e., 12 W m^{-2} at 21 bar using water and 1 M NaCl as feeds). Experimental results also suggest that inner-selective TFC hollow fiber membranes made from small dimensional fiber supports by means of delayed demixing during the fiber spinning are preferential for high pressure PRO processes. In addition, it was found that the flow rate of brine solutions plays a crucial effect on TFC membrane performance for osmotic power generation. By investigating the pressure drop as a function of flow rate, one may be able to choose appropriate PRO operation conditions to further ensure the sustainability of hollow fiber membranes for power generation.

* Corresponding author at: Department of Chemical & Biomolecular Engineering, National University of Singapore, Singapore 117576, Singapore. Tel.: +65 6516 6645; fax: +65 6779 1936.
E-mail address: chencts@nus.edu.sg (T.-S. Chung).

0306-2619/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2013.10.037

1. Introduction

The scarcity and vulnerability of current fossil fuel energy motivate other alternative, renewable, and environmentally friendly energy sources. Currently, salinity gradient energy, a clean energy from ocean and various sources of salty water, has received worldwide attention [1,2]. To effectively convert such a promising energy into electricity, pressure retarded osmosis is getting more and more interest [3,4]. Pressure retarded osmosis (PRO) is a membrane-based technique that was already proposed in the 1970s [5–7]. Although generating salinity gradient energy by PRO is theoretically feasible, the ineffective membranes used at that time made it economically infeasible. Most of early works on PRO was discontinued due to the absence of suitable PRO membranes [8,9]. Things change when forward osmosis (FO) membranes have been rapidly developed [2,10,11]. FO membranes share a similar osmotic mechanism with PRO membranes, targeting for high selectivity with high water flux and low salt flux. Thus, the recent improvement in FO membranes revives research and development for PRO processes. A Norwegian power company, Statkraft, has conducted research on salinity gradient energy since 1997 and built the first prototype plant in 2009 by mixing river water and seawater under the PRO mode. By doing so, the potential of PRO has been practically demonstrated.

To commercialize the production of osmotic energy via PRO process, a membrane power density of more than 5 W m^{-2} is crucial [3,12–14]. Besides the power density, another challenge is to have a membrane that could withstand high hydraulic pressures, since the operating pressure of the salty water compartment in the PRO process may increase up to 13 bar (for seawater) and even higher (for other highly concentrated salty water, such as RO retentate). Several studies have attempted to utilize conventional FO membranes for PRO applications [15–20]. However, without chemical or physical reinforcements, they suffer severe performance deterioration due to irreversible deformation, densification and damage when subjected to high hydraulic pressures because most FO membranes were originally designed to operate only at no or low pressures [2,17–20].

To meet the requirements of high water permeability and salt rejection, most osmotic membranes are designed to have a thin selective layer on top of a fully porous substrate. The fabrication of thin-film composite (TFC) membranes via interfacial polymerization is one of the preferred methods because it provides advantages such as availability of various moieties for interfacial polymerization, diverse tunability of supporting layer, and ease of fabrication [15–25]. Although TFC membranes with a highly porous support layer have been designed for FO applications with minimal internal concentration polarization and enhanced water permeability, they are structurally vulnerable under high pressure PRO operations. Hence, one of the major scientific challenges for material and membrane scientists is how to design a robust TFC membrane for osmotic power generation without sacrificing its high water permeability and low salt permeability.

Hollow fiber membranes have advantages of (1) high membrane area per unit membrane module volume, leading to low operating costs and high productivity, (2) self-mechanical support, preventing adverse effects of spacers used in flat-sheet membrane modules, and (3) ease of handling during fabrication and operation [26,27]. As a result, there are growing interests in using hollow fiber membranes for PRO applications [16,28]. However, the knowledge to fabricate high performance PRO hollow fiber membranes is very limited. Therefore, this work aims at revealing the science and engineering of developing a TFC hollow fiber membrane with a high water flux and good tolerance to high pressure PRO operations. The effects of spinning conditions on membrane morphology and PRO performance will also be investigated. In addition, operation condition such as flow rate also inevitably affects the mass transfer near the membrane surface and pressure drop along the flowing channel. Thus, the effects of flow rate will be studied.

P84 co-polyimide (as shown in Fig. 1) was chosen in this study as the material for the fabrication of hollow fiber membrane support because of its balanced physiochemical properties and good chemical resistance. The successful development of P84 flat-sheet membranes with good PRO performance in our previously study [29] also stimulated us to explore its potential in the hollow fiber configuration. In this work, we firstly examined the feasibility of fabricating P84 hollow fiber supports with desirable morphologies and properties via dual-layer co-extrusion technology. We then prepared TFC PRO membranes from these hollow fiber supports. Robust TFC hollow fiber membranes have been developed with superior tolerance to high pressures without compromising PRO performance.

2. Experimental

2.1. Materials and chemicals

A P84 co-polyimide (BTDA-TDI/MDI, co-polyimide of 3,3′,4,4′-benzophenone tetra-carboxylic dianhydride and 80% methylphenylene diamine + 20% methylene diamine) was purchased from HP Polymer, Austria. Fig. 1 shows its chemical structure. The solvent *N*-methyl-2-pyrrolidinone (NMP, >99.5%) and non-solvent ethylene glycol (EG, 99.9%) were ordered from Merck and VWR, respectively, and were used to prepare the spinning solutions. The de-ionized water used in experiments was produced by a Milli-Q ultrapure water system (Millipore, USA). A 50/50 wt% mixture of glycerol (Industrial grade, Aik Moh Pains & Chemicals Pte. Ltd., Singapore) and de-ionized water was prepared to post-treat as-spun hollow fiber supports before drying. Polyethylene glycol 4000, 6000, 10,000, 20,000, and 35,000 (PEG, M_w = 4000 g mol^{-1}, 6000 g mol^{-1}, 10,000 g mol^{-1}, 20,000 g mol^{-1}, and 35,000 g mol^{-1}, respectively, Sigma–Aldrich) were employed to characterize the molecular weight cut-off (MWCO), mean pore and pore size distribution of hollow fiber supports. *m*-Phenylenediamine (MPD, >99%) and 1,3,5-benzenetricarbonyl trichloride (TMC, 98%) were bought from Sigma–Aldrich. Hexane and sodium chloride (NaCl) were procured from Merck. All chemicals were used as received.

2.2. Fabrication of P84 hollow fiber supports and post-treatment

Prior to preparing polymer solutions, the P84 polymer powder was dried overnight at 90 ± 5 °C in a vacuum oven (2 mbar) to remove moisture content. The dehydrated P84 polymer was dissolved in a NMP/EG solution and Table 1 states the solution composition. After the spinning dope solution was prepared, it was degassed for several hours and then stored in a 500 mL syringe pump (ISCO Inc.) overnight before spinning. The P84 hollow fiber supports were prepared by a dry-jet wet spinning process as described in our previous publication [24]. By changing the spinning conditions, such as bore fluid composition, bore fluid flow rate, take-up speed, and spinneret dimension, four different hollow fiber membranes were spun from the same polymer solution with different morphologies and dimensions. All nascent fibers did not experience additional extra drawing (i.e., no extension) after leaving the spinneret, which means that the take-up speed of the hollow fibers was almost the same as the falling speed into the coagulation bath. Two dual-layer spinnerets illustrated in Fig. 2 were employed in this work and Table 1 tabulates the spinning conditions. The spinning dope was conveyed through the middle channel, while NMP was transported via the outer channel in order to induce delayed demixing at the outer membrane surface. After