



# Design of robust hollow fiber membranes with high power density for osmotic energy production



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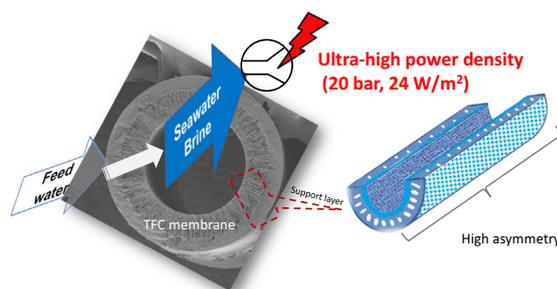
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## HIGHLIGHTS

- PES TFC hollow fibers were fabricated for pressure retarded osmosis.
- Different macro-structures were found on the hollow fibers.
- Fibers' micro-structure determined the mechanical strength and power density.
- 24.3 W/m<sup>2</sup> was produced using 1 M NaCl and DI water.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study highlights the design strategy of highly asymmetric hollow fiber membranes that possess both characteristics of high flux and high mechanical strength to effectively reap the osmotic energy from seawater brine with an ultrahigh power density. An advanced co-extrusion technology was employed to fabricate the polyethersulfone (PES) hollow fiber supports with diversified structures from macrovoid to sponge-like. The microstructure of the supports is found critical for the stability and water permeability of the thin film composite (TFC) membranes. A high porosity in the porous layer is needed to reduce internal concentration polarization, while a thick and relatively dense skin layer underneath the TFC layer is required to maintain good mechanical stability and stress dissipation. The pore size of the supporting layer underneath the TFC layer must be small with a narrow pore size distribution to ensure the formation of a less-defective, highly permeable and mechanically stable TFC layer. The newly developed hollow fiber comprising high asymmetry, high porosity, and a thick skin layer with a small and narrow pore size distribution underneath the TFC layer produces a maximum power density of 24.3 W/m<sup>2</sup> at 20.0 bar by using 1 M NaCl as the concentrated brine and deionized (DI) water as the feed. The proposed design strategy for ultrahigh power density membranes clearly advances the osmotic energy production close to commercialization with a quite cost-effective and practicable approach.

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## 1. Introduction

Clean and renewable energy sources have received the highest priority for the exploration of sustainable power supplies in today's world. Osmotic power, the salinity gradient energy which

conserves the highest energy concentration of all the marine sources, has attracted intense research interests in recent years [1–3]. The average osmotic pressure of seawater is 27 atm, equivalent to the pressure of a water head of around 280 m. The extent of such energy in the ocean is estimated to be 1750–2000 TW h per year [1]. If concentrated brine and brackish water are taken into account, the global total osmotic power becomes even higher.

Pressure retarded osmosis (PRO) is a clean and environmental friendly process that harvests osmotic energy across a

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### Nomenclature

|            |  |                   |                                     |
|------------|--|-------------------|-------------------------------------|
| $A$        | water permeability, $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ , abbreviated as LMH/bar | $R$               | solute rejection                    |
| $A_m$      | effective membrane surface area, $\text{m}^2$  | $S$               | membrane structural parameter, m    |
| $B$        | salt permeability, $\text{L m}^{-2} \text{h}^{-1}$ , abbreviated as LMH                      | $SF$              | safety factor                       |
| $Cd_f$     | feed conductivity, $\mu\text{s/cm}$  | $T$               | maximal tensile strength, MPa       |
| $Cd_p$     | permeate conductivity, $\mu\text{s/cm}$  | TFC               | thin-film-composite                 |
| $d_p$      | pore diameter, m   | $W$               | power density, $\text{W/m}^2$       |
| $d_s$      | solute diameter, m   | $\varepsilon$     | membrane porosity                   |
| $D$        | diffusion coefficient of salt in the membrane substrate, $\text{m}^2 \text{s}^{-1}$          | $\tau$            | membrane tortuosity                 |
| FO         | forward osmosis  | $\chi$            | membrane thickness, m               |
| $i$        | van't Hoff factor  | $\pi$             | osmotic pressure, bar               |
| $ID$       | inner diameter, m  | $\rho_p$          | polymer density, $\text{g cm}^{-3}$ |
| $J_s$      | reverse salt flux, $\text{g m}^{-2} \text{h}^{-1}$   | $\mu_p$           | mean effective pore diameter, m     |
| $J_w$      | water flux, $\text{L m}^{-2} \text{h}^{-1}$  | $\sigma_p$        | geometric standard deviation        |
| $l$        | fiber length, cm   |                   |                                     |
| $m$        | membrane weight, g   | <b>Subscripts</b> |                                     |
| $M$        | molecular weight   | $b$               | bulk solution                       |
| $M_s$      | solute molecular weight  | $D$               | draw solution side                  |
| $OD$       | outer diameter, m  | $F$               | feed solution side                  |
| PRO        | pressure retarded osmosis  | $P$               | permeate                            |
| $\Delta P$ | hydraulic pressure difference, bar   | $w$               | water                               |
| $P$        | burst pressure, bar  | $s$               | solute                              |
| $Q$        | water permeation volumetric flow rate, $\text{L h}^{-1}$                                     | $p$               | pore                                |

semipermeable membrane between two solutions of different osmotic pressures. Since water transports naturally from the dilute solution to the concentrated solution (referred to as draw solution thereafter) across the semipermeable membrane, the pressure of the draw solution will be increased in its compartment that would drive the hydroturbine connected to its outlet. The work from the inflow of the permeated water is therefore converted to electricity by the hydroturbine. The technical and economic feasibility of PRO for power generation were investigated in 1970s [4–6]. However, the obtained energy was far below expectation due to unsuitable reverse osmosis (RO) membranes and membrane modules [7–9]. The development of PRO for power generation was retarded for a long time owing to the lack of efficient membranes.

In 2009, Statkraft built the first PRO prototype plant in Norway and demonstrated power densities of less than  $1.5 \text{ W/m}^2$  using conventional cellulose acetate membranes [3,10]. This value is far below the target power density of  $5 \text{ W/m}^2$  for the process to be commercially viable [11,12]. However, the rapid progress in forward osmosis (FO) membranes [13–15] opened up new perspectives for the development of PRO membranes [16–23]. Experiments with cellulose triacetate-based Hydration Technology Innovations (HTI) membranes achieved a maximum power density of  $5.06 \text{ W/m}^2$  when concentrated brine (1.03 M NaCl) was used as the draw solution [16]. Yip et al. prepared thin film composite (TFC) flat-sheet membranes that could theoretically produce a peak power density of  $9.21 \text{ W/m}^2$  by using seawater and river water as feeds [17]. However, no high pressure PRO tests were conducted. Chou et al. developed TFC hollow fiber membranes with a power density of  $10.6 \text{ W/m}^2$  using 1 M NaCl seawater brine and 40 mM NaCl wastewater as feeds, but their hollow fibers can only withstand a hydraulic pressure of less than 10 bar [18].

To understand the causes of low power density and low operation pressure, fundamentals were conducted by Zhang et al. and Li et al. to examine the effects of pre-compression of membrane substrates and post-treatment of TFC layers on PRO performance [19,20]. A TFC flat-sheet membrane with a peak power density up to  $12.0 \text{ W/m}^2$  was therefore demonstrated at 15 bar using 1 M

NaCl as the feed [21]. Recently, a TFC hollow fiber membrane exhibiting a peak power density of  $14 \text{ W/m}^2$  at 16 bar was developed by Han et al. using 1 M NaCl seawater brine and deionized water as feeds [22], while a TFC flat-sheet membrane made of nanofiber substrates with a power density of  $15.2 \text{ W/m}^2$  at 15.2 bar was established by Song et al. using 1.06 M NaCl and 0.9 mM NaCl as feeds [23]. However, both membranes cannot withstand a trans-membrane pressure higher than 16 bar.

Apart from seawater, the concentrated seawater brine from desalination plants is also an attractive source for osmotic power generation, which may not only provide the electricity for the desalination process, but also solve the problem of brine disposal [19,23]. Ideally, the optimum operation pressure for the production of salinity gradient energy is one half the osmotic pressure of the concentrated brine, i.e., around 23 bar for 1 M NaCl. Both lab-scale [24] and pilot-plant experiences [25] revealed that the feed spacers for flat sheet membrane modules not only decrease water flux and increase channel pressure, but also cause severe fouling. Additional efforts are needed to design PRO modules made of flat-sheet membranes because the current design for spiral wound RO modules is not suitable [25,26]. In contrast, hollow fiber membranes are characterized by their self-supporting properties and high packing density [27]. Since no feed spacer is involved, a lower minimum power density is required for hollow fibers than flat sheet membranes for the PRO process to be commercially viable [11,12]. Therefore, advancing hollow fiber membrane performance with a much higher withstanding pressure and power density is essential for the PRO commercialization. The ideal PRO membrane must possess the following characteristics: (1) high water permeability; (2) reasonably low internal concentration polarization; (3) good mechanical strength and (4) reasonably low salt permeability.

This study not only aims to reveal the design strategies for ultrahigh performance TFC hollow fiber membranes for osmotic power generation but also elucidate the basic science and engineering behind it. Fibers with remarkably different macro-scale morphologies were designed through the advanced co-extrusion

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