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Conceptual demonstration of novel closed-loop pressure retarded osmosis process for sustainable osmotic energy generation

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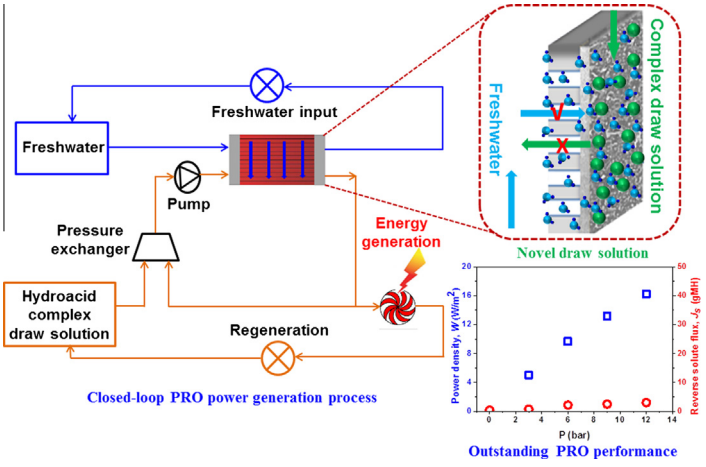
HIGHLIGHTS

- One novel closed-loop PRO process was demonstrated for osmotic energy capture for the first time.
- Highly robust and permeable PRO hollow fiber membrane was developed.
- Hydroacid complex draw solute with high water flux and negligible reverse solute flux was synthesized.
- Power density of 16.2 W/m^2 with an ultralow reverse solute flux (J_s/J_w < 0.062 g L^{-1}) was achieved at 12 bar.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, one novel closed-loop pressure retarded osmosis (PRO) process promoted by an effective hydroacid complex draw solution has been demonstrated for harvesting the renewable salinity-gradient energy. The complex draw solute was molecularly constructed to possess unique characteristics of high osmotic pressure, large molecular size and relative low viscosity, and easy regeneration. Compared to conventional PRO processes, the newly developed closed-loop PRO process exhibits promising advantages of sustainable high power output, negligible internal concentration polarization and low membrane fouling, as well as no problems of feed water pretreatment and brackish water discharge. Employing a highly permeable (A = 4.30 LMH/bar) and selective (B = 0.47 LMH) thin film composite PRO hollow fiber membrane, a power density of 16.2 W/m^2 can be achieved with an ultralow reverse solute flux (J_s/J_w < 0.062 g L^{-1}) at 12 bar when using 1 M complex draw solution and deionized water as feeds. The diluted complex draw solution can be regenerated via a solvent precipitation process, and the outstanding PRO performance could be almost fully recovered. We believe the newly developed closed-loop PRO process shows great potential for salinity-gradient energy capture, although the specific benefits have to be fully defined through energy or cost analysis.

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1. Introduction

By using a semi-permeable membrane to control the mixing of solutions with different salinities, pressure retarded osmosis (PRO) has emerged as one of the most effective processes to harvest the renewable salinity-gradient energy (or osmotic power) in terms of electricity without causing adverse environmental impacts [1–7]. The global estimation of this osmotic power is 2.6 TW/year, and the value could be higher if the osmotic energy harvested from the high salinity retentate such as reverse osmosis (RO) desalination plants is taken into account [3,8]. However, utilization of PRO for practical power supply is still facing many difficulties such as the absence of the specialized PRO membrane, internal concentration polarization (ICP), membrane fouling, feed water pretreatment and energy consumption in the energy recovery device [3–8].

Recently, lots of effective flat-sheet and hollow fiber PRO membranes have been successfully developed [9–16]. Song et al. made a flat-sheet thin film composite (TFC) PRO membrane based on nanofiber substrate and obtained a power density of 15.2 W/m^2 at 15.2 bar by employing 1.06 M NaCl as the draw solution and 0.9 mM NaCl as the feed [11]. Zhang et al. invented one TFC PRO hollow fiber membrane which can produce a power density of 24.0 W/m^2 at 20.0 bar using 1 M NaCl as the concentrated brine [14]. Compared to flat-sheet membranes, the self-supported hollow fiber PRO membranes are of great interest due to the high surface to volume ratio and spacer-free module fabrication. Not only could this minimize the membrane deformation [17], but also eliminate the extra energy loss in the feed flow channel of flat-sheet membrane modules [17–19].

However, some disadvantages have been observed in conventional PRO power generation processes. One of them is the requirement of effectively pretreating the feed waters in order to prevent membrane fouling, which would significantly increase the process costs [8]. Another disadvantage arises from the low osmotic pressure gradient between the natural feed water streams such as seawater and river water. As a result, there are no sufficiently high hydraulic pressures available for efficient power generation. In case the feed water contains a large amount of salts, the process efficiency would be diminished because of the dramatically amplified ICP and salt leakage [20]. The severe reverse salt flux across the PRO membrane is another shortcoming, which would induce other potential problems such as enhanced ICP, reduced driving force, exacerbated membrane fouling, and increased downstream processing. Furthermore, it would be difficult or impossible to operate the conventional PRO process in countries or areas with severe water shortages. These negative facts on the conventional PRO process have triggered the exploration of other novel PRO processes such as the closed-loop PRO [20–22]. Closed-loop PRO is a promising process for salinity gradient energy generation which still employs osmotic pressure as a medium but is no longer from natural streams. Therefore, the aforementioned shortcomings faced by the conventional PRO could be minimized or overcome by optimizing the draw solution and feed solution. The primary challenges to current closed-loop PRO process are the low power output and the low thermal efficiency since intensive energy input may be required for draw solution regeneration.

In this study, a novel closed-loop PRO process is conceptually demonstrated to harvest the osmotic energy in terms of electricity. A molecularly designed hydroacid complex draw solution and freshwater resources with low salinities are used as the working fluids to maximize the membrane mass transfer. The complex draw solution possesses a high osmotic pressure, negligible reverse solute flux, and easy approaches in regeneration. The feasibility of the newly developed PRO process for power generation is studied in terms of water flux, power density and reverse solute flux by using a robust highly permeable TFC PRO hollow fiber membrane.

2. Experimental

2.1. Materials and chemicals

Matrimid® 5218 purchased from Vantico Inc. was used as the polymer material to fabricate the hollow fiber membrane substrate. N-methyl-2-pyrrolidone (NMP, >99.5%) and diethylene glycol (DEG, >99.0%) from Merck were utilized as the solvent and additive in the membrane fabrication, respectively. Polyethylene glycol with different molecule weights was ordered from Sigma–Aldrich to characterize the pore characteristics and molecular weight cut-off (MWCO) of the hollow fiber substrate. 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 the hollow fiber substrate before drying. Trimesoyl chloride (TMC, >98%) and m-phenylenediamine (MPD, >99%) from Sigma–Aldrich were employed as the monomers for the interfacial polymerization reaction. Sodium dodecyl sulphate (SDS, >97%, Fluka) and triethylamine (TEA, >99%, Sigma–Aldrich) were used as additives, while hexane (>99.9%, Fisher Chemicals) as the solvent for the TMC solution. $Fe(NO_3)_3{\cdot}9H_2O$ (99%), citric acid (99%) and NaOH (99%) were purchased from Sigma–Aldrich for the synthesis of hydroacid complex draw solute. Ethanol (EtOH, 99%) was purchased from Acros Organics to regenerate the complex draw solute. The deionized (DI) water was produced by a Milli-Q unit (Millipore) with a resistivity of 15 MΩ cm.

2.2. Fabrication of hollow fiber membrane substrate

The hollow fiber membrane support for TFC PRO membranes was fabricated via a wet–wet phase inversion spinning process. In order to obtain the desirable membrane structure and morphology during membrane formation, the dual-bath coagulation spinning process using a single-layer spinneret was employed to effectively control the phase inversion [13,23]. Table 1 summarizes the detailed spinning conditions of the hollow fiber substrate. The hollow fiber spinning was repeated for three times to ensure the membrane reproducibility.

For module fabrication, the hollow fiber membranes were assembled into a module holder which consists of two Swagelok stainless steel male run tees connected by a perfluoroalkoxy tube 3/8 in. in diameter. Both ends were sealed with a slow cure epoxy resin (KS Bond EP231, Bondtec).

2.3. Fabrication of the TFC PRO hollow fiber membrane

A polyamide selective skin was formed on the inner surface (lumen side) of the hollow fiber substrate via interfacial polymerization. As illustrated in our previous work [24–26], a 2 wt.% MPD aqueous solution containing 0.5 wt.% TEA and 0.1 wt.% SDS was

Table 1
Spinning conditions of hollow fiber membrane substrate.

Spinning parameter	Hollow fiber membrane substrate
Polymer dope solution (wt.%)	16.9/17/65.3/0.8 Marimid/DEG/NMP/H_2O
Bore-fluid solution (wt.%)	H_2O/NMP 70:30
Polymer dope flow rate (ml/min)	1.5
Bore-fluid flow rate (ml/min)	0.75
Air–gap length (cm)	2.0
Take-up speed (m/min)	2.5 (free fall)
External coagulant	IPA/Water (60/40 wt.%) then Tap water dual bathes of coagulation
Spinneret dimension (mm)	Single-layer spinneret (1.2–0.68–0.48)
Spinning temperature (°C)	Ambient (23 °C ± 2)
Post treatment	50/50 wt.% glycerol/water for 2 days