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Osmotic Power Generation by Inner Selective Hollow Fiber Membranes: An investigation of thermodynamics, mass transfer, and module scale modelling

Jun Ying Xiong ^a, Dong Jun Cai ^b, Qing Yu Chong ^a, Swin Hui Lee ^a, Tai-Shung Chung ^{a,c,*}

^a Department of Chemical and Biomolecular Engineering, National University of Singapore,
4 Engineering Drive 4, Singapore 117585, Singapore

^b Department of Electrical and Computer Engineering, National University of Singapore, 4
Engineering Drive 3, Singapore 117583, Singapore

^c Water Desalination & Reuse (WDR) Center, King Abdullah University of Science and
Technology, Thuwal 23955-6900, Saudi Arabia

* Corresponding author: Tel.: +65 6516 6645, Email: chencts@nus.edu.sg

Abstract

A comprehensive analysis of fluid motion, mass transport, thermodynamics and power generation during pressure retarded osmotic (PRO) processes was conducted. This work aims to (1) elucidate the fundamental relationship among various membrane properties and operation parameters and (2) analyse their individual and combined impacts on PRO module performance. A state-of-the-art inner-selective thin-film composite (TFC) hollow fiber membrane was employed in the modelling. The analyses of mass transfer and Gibbs free energy of mixing indicate that the asymmetric nature of hollow fibers results in more significant external concentration polarization (ECP) in the lumen side of the inner-selective hollow fiber membranes. In addition, a trade-off relationship exists between the power density (*PD*) and the specific energy (*SE*). The *PD* vs. *SE* trade-off upper bound may provide a useful guidance whether the flowrates of the feed and draw solutions should be further optimized in order to (1) minimize the boundary thickness and (2) maximize the osmotic power generation. Two new terms, mass transfer efficiency and power harvesting efficiency

for osmotic power generation, have been proposed. This work may provide useful insights to design and operate PRO modules with enhanced performance so that the PRO process becomes more promising in real applications in the near future.

Keywords:

Pressure retarded osmosis (PRO), hollow fiber membrane, Gibbs free energy of mixing, mass transfer, module scale simulation

Nomenclature

ECP	external concentration polarization
ICP	internal concentration polarization
PRO	pressure retarded osmosis
TFC	thin film composite
A	water permeability (LMH/bar)
A_m	effective membrane area (m^2)
A_{shell}	the cross-sectional area of the cross-section in the shell side (m^2)
B	reverse salt permeability (LMH)
$C_{D,b}$	salinity of the bulk draw solution (M)
$C_{D,m}$	surface salinity of the selective layer at the draw solution side (M)
C_f	salt concentration of the feed (M)
$C_{F,b}$	salinity of the bulk feed solution (M)
$C_{F,m}$	surface salinity of the selective layer at the feed side (M)
$C_{F,t}$	salinity at the external surface of hollow fibers facing the feed (M)
ΔC_m	salinity gradient across the selective layer of the membrane (M)
d_f	boundary layer thickness of the ECP layer at the feed side (m)
d_i	inner diameter of hollow fibers (m)
d_{module}	inner diameter of PRO modules (m)
d_o	outer diameter of hollow fibers (m)
d_s	boundary layer thickness of the ECP layer at the draw solution side (m)
dP_i	pressure drop at stage i (Pa)
D	salt diffusivity in water (m^2/s)
D_e	the effective salt diffusivity (m^2/s)
F_{ICP}	ICP factor of the porous support (-)
$F_{ECP,f}$	ECP factor of the feed solution side (-)
$F_{ECP,s}$	ECP factor of the draw solution side (-)
G	molar Gibbs free energy (J/mol)
ΔG_M	molar Gibbs free energy of mixing (J/mol)
ΔG_V	specific Gibbs free energy of mixing (kWh/m^3)
J_w	water flux (LMH)

J_s	reverse salt flux (gMH)
J_s/J_w	specific reverse salt flux (i.e., equivalent concentration) (M)
k	mass-transfer coefficient (m/s)
L	length of hollow fibers (m)
m_A	molality of NaCl in the solution (mol/kg-H ₂ O)
m_D	molality of NaCl in the draw solution (mol/kg-H ₂ O)
m_F	molality of NaCl in the feed solution (mol/kg-H ₂ O)
$m_{\pm}$	mean ionic molality of the salt (mol/kg- H ₂ O)
n	total number of the stages of PRO modules (-)
N	total number of hollow fibers packed in PRO modules (-)
p_{shell}	the wetted perimeter of the cross-section in the shell side (i.e., feed side) (M)
PD	power density (W/m ²)
ΔP	operation pressure (bar)
ΔP_i	local pressure difference across the membrane (bar)
Q_d	draw solution flow rate (m ³ /s)
$Q_{d,avg,i}$	local average draw solution flow rate at stage i (m ³ /s)
r	radial position within hollow fiber membranes (m)
r_i	inner radius of hollow fibres (m)
r_o	outer radius of hollow fibres (m)
R	universal gas constant (0.083145 L.bar.mol ⁻¹ .K ⁻¹)
Re	Reynolds number (-)
S	Membrane structural parameter (-)
Sc	Schmidt number (-)
Sh	Sherwood number (-)
T	absolute temperature (K)
TMP	trans-membrane pressure (bar)
u_{lumen}	velocity of the draw solution within hollow fibers (m/s)
x	certain normalized position of the PRO module at the longitudinal direction (-)
x_A	mole fraction of the solute (i.e., NaCl) (-)
x_B	mole fraction of the solvent (i.e., water) (-)
ρ	density of the draw solution (kg/m ³)
μ	the kinetic viscosity of the draw solution (cP)
μ_A^0	chemical potential of the salt in solutions at its standard status (J/mol)
μ_B^0	chemical potential of the pure water (J/mol)
μ^d	chemical potential of the draw solution (J/mol)
μ^f	chemical potential of the feed solution (J/mol)
μ^M	chemical potential of the mixed solution (J/mol)
Φ	mole fraction of the draw solution part in the mixed solution (-)
ν	Van't Hoff coefficient for the strong electrolytes ($\gamma = 2$ for NaCl)
$\gamma_{\pm}$	mean ionic activity coefficient based on $m_{\pm}$ (-)
π	osmotic pressure (bar)
$\Delta\pi$	osmotic pressure difference across the membrane (bar)
$\Delta\pi_b$	osmotic pressure difference between the bulk draw solution and the bulk feed solution (bar)
π_D	osmotic pressure of the bulk draw solution (bar)
$\pi_{D,m}$	osmotic pressure of at selective layer surface on the draw solution side (bar)
$\Delta\pi_{eff}$	effective osmotic pressure difference across the selective layer of hollow fiber membranes (bar)
π_F	osmotic pressure of the bulk feed solution (bar)
$\pi_{F,m}$	osmotic pressure of at selective layer surface on the feed side (bar)

φ	porosity of the porous support (-)
τ	tortuosity of the porous support layer (-)
ϕ_F	feed mole fraction

Superscript

M	mixed solution
d	draw solution
f	feed solution

Subscript

A	the salt (i.e., NaCl)
B	the solvent (i.e., water)
<i>lumen</i>	lumen side of hollow fibers (i.e., draw solution side)
<i>shell</i>	shell side of hollow fibers (i.e., feed solution side)

Introduction

There has been growing attention towards pressure retarded osmosis (PRO) as a form of green energy technology [1-10]. PRO is a process to harvest osmotic energy by using a semipermeable membrane between a low salinity feed (referred to as “the feed” thereafter) and a high salinity draw solution [3-7]. When the transmembrane pressure is less than the osmotic gradient across the membrane, water will spontaneously permeate from the low salinity side to the high salinity side. Osmotic energy can be generated when releasing the pressure and water volume built up in the draw solution compartment via energy exchangers or hydraulic turbines [1-10]. The power density of the PRO membrane is a product of water flux and transmembrane pressure. PRO is a sustainable green energy technology because it does not emit greenhouse gases and chemicals.

To move the PRO technology closer to commercialization, many advanced PRO membranes have been developed in recent years [7,11-25], significant progresses have also been made to understand PRO from three aspects; namely, (1) the thermodynamics of mixing between the draw and feed solutions, (2) the mass transfer across PRO membranes, and (3) the simulation of PRO modules [7-13, 17, 26-34]. Lin et al. studied the thermodynamic limits of extractable energy from PRO [26]. A module scale analysis was conducted to investigate the thermodynamic limits of system performance by deliberately ignoring non-ideal factors such as reverse salt flux, internal and external concentration polarization (i.e., ICP and ECP, respectively). Yip et al. studied the mass transfer of water flux across flat sheet membranes [13] and found ECP on the draw solution side to be significant for thin-film composite (TFC) membranes. She et al. examined the water and solute transport of flat sheet membranes under forward osmosis (FO) and PRO, and elaborated the factors and mechanisms governing the fouling behaviour [27]. Different from those theoretical modelling approaches, Efraty derived

a simplified but effective model for water flux in which all the detrimental factors such as ICP, ECP, and reverse salt flux were incorporated in one factor characterized by the FO actual/ideal flux ratio [28]. The simplified water flux equation was able to model the single-stage PRO module and describe the distinction between power density (PD) and net electric power density ($NEPD$).

In terms of modelling the mass transport across PRO hollow fiber membranes, Zhang and Chung investigated the instant and accumulative effects of salt permeability of thin-film composite (TFC) polyethersulfone (PES) hollow fiber membranes on PRO performance by using the water flux equation developed mainly for the flat sheet configuration [12]. They found that a lower salt permeability B is essential to maximize the power density. Xiong et al. also elaborated the flux reduction behaviour of PRO hollow fiber membranes by employing one-dimensional mass transfer equations [30]. Wan and Chung evaluated the energy recovery for three distinct PRO systems by using the water flux equation for flat sheet membranes and considering ECP on the draw solution side [31]. Zhang and Chung further analysed the net energy output and discussed the optimal operation conditions at the module scale based on the currently available PRO hollow fiber membranes using the one-dimensional water flux equation [32]. Different from others, Sivertsen et al. were the pioneers in developing a mass transport model for PRO in cylindrical coordinates [33] and examined the PRO efficiency for outer-selective hollow fiber membrane modules [34]. Both ECP in the feed and draw solution sides were considered in their study.

Although prior works have studied the PRO process from various aspects and configurations, no work has combined the aforementioned three aspects to systematically investigate the

PRO performance based on the start-of-the-art inner-selective hollow fiber membranes. Therefore, this work aims to elaborate various operation parameters and their impacts on PRO module performance by employing thermodynamics, mass transfer across membranes in cylindrical coordinates, and PRO module simulation. High performance inner-selective TFC hollow fiber membranes recently developed in our group [7, 11, 12, 17] were employed in the modelling work to examine how the interactions among the fundamental internal factors affect the behaviour of the external performance. The insights obtained from the specific Gibbs free energy of mixing and mass transfer across PRO hollow fiber membranes are applied in PRO module simulations to expand our knowledge of the operation of PRO modules. This work may provide useful insights to design next-generation PRO modules with enhanced performance in the near future.

1. Theory

2.1 Gibbs free energy of mixing

The molar Gibbs free energy of mixing, ΔG_M , is defined as the energy per mole of the mixed solution obtained from mixing two solutions with different solute concentrations in an isothermal and isobaric process [35]:

$$-\Delta G_M = G^M - [\Phi G^d + (1 - \Phi) G^f] \quad (1)$$

in which G^M , G^d , G^f are the molar Gibbs free energy of the mixed, draw, and feed solutions, respectively. Φ is the mole fraction of the draw solution in the mixed solution. The molar Gibbs free energy of the mixed, draw, and feed solutions can be described as:

$$G = x_A \mu_A + x_B \mu_B \quad (2)$$

in which A and B denote the solute and solvent, respectively. x_A and x_B are the mole fractions of the solute and solvent, respectively. μ_A and μ_B are the chemical potentials of the solute and solvent, respectively. Many substances may be dissolved in water to generate the solute

gradient for the harvest of osmotic power. In this study, a single strong electrolyte (sodium chloride, NaCl) is employed. For the aqueous NaCl solution, the chemical potential of NaCl can be calculated as follows [36]:

$$\mu_A = \mu_A^0 + \nu RT \ln(m_{\pm} \gamma_{\pm}) \quad (3)$$

in which R is the ideal gas constant and T is the absolute temperature; μ_A^0 is the chemical potential corresponding to the standard state; $m_{\pm}$ is the mean ionic molality and $\gamma_{\pm}$ is the mean ionic activity coefficient. ν is the van't Hoff factor for the electrolyte ($\nu=2$ for NaCl). The chemical potential of water in the dilute aqueous NaCl solution can be estimated as:

$$\mu_B = \mu_B^0 + RT \ln(x_B) \quad (4)$$

in which μ_B^0 is the chemical potential of the pure water, and x_B is the mole fraction of water in the solution.

Combining Eq. 1 to Eq. 4, we can have:

$$-\frac{\Delta G_M}{RT} = [2x_A^M \ln(m_{\pm}^M \gamma_{\pm}^M) + x_B^M \ln(x_B^M)] - \{\Phi [2x_A^d \ln(m_{\pm}^d \gamma_{\pm}^d) + x_B^d \ln(x_B^d)] + (1 - \Phi) [2x_A^f \ln(m_{\pm}^f \gamma_{\pm}^f) + x_B^f \ln(x_B^f)]\} \quad (5)$$

For aqueous NaCl solutions, the mean ionic molality of NaCl is equal to the molality of NaCl (i.e., m_A) in the solution. The mean ionic activity coefficient $\gamma_{\pm}$ can be readily found in the literatures [36, 37]. To facilitate the later module scale analysis, it is more convenient to use the specific Gibbs free energy of mixing ΔG_V instead of ΔG_M . The specific Gibbs free energy of mixing ΔG_V is defined as energy per unit volume of the mixed solution generated from mixing two solutions of different salinities in an isothermal and isobaric process. As the salinities of interest in this study are relatively low, ΔG_M can be easily converted to ΔG_V by assuming negligible contribution of the solute to the solution volume.

2.2 Mass Transfer in PRO hollow fiber membranes

Before developing the governing equations for a PRO module, basic mass transfer equations across a PRO membrane is briefly highlighted. A schematic illustration of the salt concentration profile across an inner-selective PRO hollow fiber membrane is given in Fig. 1. r_i is the inner radius of hollow fibres. d_s and d_f are the boundary layer thicknesses at the draw solution and feed solution sides, respectively. At any radial position between $r_i - d_s$ and $r_o + d_f$, the salt flux J_s across this position comprises two components: a diffusive component due to the salt concentration gradient, and a convective component due to the bulk flow induced by the water flux J_w [38, 39]

$$J_s = -D \frac{dC(r)}{dr} - J_w C(r) \quad (6)$$

where D is the salt diffusivity. Eq. 6 can be rearranged as [33, 34]:

$$\frac{J_s}{J_w} = -\frac{D}{J_w} \frac{dC(r)}{dr} - C(r) \quad (7)$$

J_w will not be constant with respect to the position r because the available flow area changes in the radial direction. J_w can be related to the water flux at the membrane internal surface $J_w(r_i)$ by:

$$J_w \cdot 2\pi r = J_w(r_i) \cdot 2\pi r_i \quad (8)$$

And therefore,

$$J_w = J_w(r_i) \frac{r_i}{r} \quad (9)$$

Substituting Eq. 9 into Eq. 7 gives:

$$\frac{J_s}{J_w} = -\frac{D}{J_w(r_i)r_i} \cdot r \frac{dC(r)}{dr} - C(r) \quad (10)$$

At steady state, no accumulation of water and salt occurs in the porous support and the boundary layers, J_s/J_w is thus constant and independent of the radial position r . Eq. 10 can therefore be rearranged as:

$$\frac{dC(r)}{C(r) + \frac{J_s}{J_w}} = -\frac{J_w(r_i)r_i}{D} \cdot \frac{dr}{r} \quad (11)$$

Integration of Eq. 11 gives:

$$\ln\left(C(r) + \frac{J_s}{J_w}\right) = -\frac{J_w(r_i)r_i}{D} \ln(r) \quad (12)$$

Eq. 12 serves as the general equation which can be applied to both the porous support and the boundary layers on the feed and draw solution sides. When Eq. 12 is applied to the boundary layer on the draw solution side, the following is obtained:

$$C_{D,m} = C_{D,b} \left(\frac{r_i - d_s}{r_i}\right)^{\frac{J_w(r_i)r_i}{D}} + \frac{J_s}{J_w} \left[\left(\frac{r_i - d_s}{r_i}\right)^{\frac{J_w(r_i)r_i}{D}} - 1 \right] \quad (13)$$

The ECP factor of the draw solution side ($F_{ECP,s}$) can be defined as:

$$F_{ECP,s} = \left(\frac{r_i - d_s}{r_i}\right)^{\frac{J_w(r_i)r_i}{D}} \quad (14)$$

Then Eq. 13 can be simplified to:

$$C_{D,m} = C_{D,b} F_{ECP,s} + \frac{J_s}{J_w} (F_{ECP,s} - 1) \quad (15)$$

Similarly, when Eq. 12 is applied to the porous support and the boundary layer on the feed side, it gives:

$$C_{F,m} = C_{F,t} F_{ICP} + \frac{J_s}{J_w} (F_{ICP} - 1) \quad (16)$$

$$C_{F,t} = C_{F,b} F_{ECP,f} + \frac{J_s}{J_w} (F_{ECP,f} - 1) \quad (17)$$

Where F_{ICP} and $F_{ECP,f}$ are the ICP factor of the porous support and ECP factor of the feed side, respectively:

$$F_{ICP} = \left(\frac{r_0}{r_i}\right)^{\frac{J_w(r_i)r_i}{D_e}} \quad (18)$$

$$F_{ECP,f} = \left(\frac{r_0+d_f}{r_0}\right)^{\frac{J_w(r_i)r_i}{D}} \quad (19)$$

In which D_e in Eq. 18 is the effective salt diffusivity defined as follows:

$$D_e = D \cdot \frac{\varphi}{\tau} \quad (20)$$

Where φ and τ are the porosity and tortuosity of the porous support, respectively.

The water flux across the selective layer can be computed as follows [38, 40]:

$$J_w(r_i) = A(\Delta\pi_{eff} - \Delta P) = A(\pi_{D,m} - \pi_{F,m} - \Delta P) \quad (21)$$

in which A is the water permeability; ΔP is the operation pressure; $\pi_{F,m}$ and $\pi_{D,m}$ are the osmotic pressures at the selective layer surfaces (Fig. 1). As the salinity of the feed and draw solutions in this study is reasonably low (i.e., up to 1.2M NaCl), $\pi_{D,m}$ and $\pi_{F,m}$ can be calculated using the van't Hoff equation [31, 32]:

$$\pi = \gamma \cdot R \cdot T \cdot C \quad (22)$$

in which γ is the van't Hoff factor for the electrolytes ($\gamma = 2$ for NaCl); C is the concentration of the feed or draw solution. On the other hand, the salt flux across the selective layer J_s can be written as [38]:

$$J_s(r_i) = B(C_{D,m} - C_{F,m}) \quad (23)$$

in which B is the salt permeability; $C_{F,m}$ and $C_{D,m}$ are the salt concentrations of the feed and draw solutions at the selective layer surfaces (Fig. 1), respectively.

Eq. 13 to Eq. 23 serve as the governing equations used to calculate PRO performance at the membrane level. Once the membrane intrinsic properties (i.e., A , B , and S), membrane configuration parameters (i.e., r_i and r_o) and operation parameters (i.e., $C_{D,b}$, $C_{F,b}$, ΔP , d_s , d_f) are given, the water flux J_w and reverse salt flux J_s can be obtained based on the governing equations. The power density PD is determined by:

$$PD = \frac{J_w \Delta P}{36} \quad (24)$$

in which J_w is the water flux in the unit of LMH, ΔP is the operation pressure in the unit of bar, and PD is the power density in the unit of W/m². The maximal water flux can be determined by the bulk salinity gradient without considering ICP and ECP effects:

$$J_w^{max} = A(\Delta\pi_b - \Delta P) \quad (25)$$

in which $\Delta\pi_b$ is the osmotic pressure difference between the bulk draw solution and the bulk feed solution (Fig. 1). $\Delta\pi_b$ can be calculated using $C_{D,b}$ and $C_{F,b}$ based on Eq. 22. The maximal power density can therefore be obtained as follows:

$$PD_{max} = \frac{A(\Delta\pi_b - \Delta P)\Delta P}{36} \quad (26)$$

2.3 Modeling of PRO hollow fiber membrane modules

As counter-current flow normally achieves higher efficiency in the harvest of osmotic power, a counter-current mode is adopted in this study. In PRO modules, salinities and flowrates of the feed and draw solutions continuously change along the flow channels within the module due to the water permeation and reverse salt diffusion. As illustrated in Fig. 2, a hollow fiber module operated under the counter-current flow mode can be divided into a series of stages. The details of stage i are magnified in Fig. 2e. When the membrane intrinsic properties (i.e., A , B , and S), membrane configuration parameters (i.e., r_i and r_o) and the local operation

parameters (i.e., $C_{D,b,i}$, $C_{F,b,i}$, ΔP_i , $d_{s,i}$, $d_{f,i}$) are known, the local membrane performance such as water flux $J_{w,i}$, reverse salt flux $J_{s,i}$, power density PD_i , and the maximal power density $PD_{i,max}$ can be obtained based on the governing equations Eq. 13 to Eq. 26 given in section 2.2.

2.3.1 Determination of local operation parameters

The local operation parameters are determined in the following manner. The pressure drop in the shell side of the modules is normally negligible due to its large dimension. However, there is a pressure drop inside the fiber lumen due to the friction between the lumen wall and the draw solution. As the flow of the draw solution inside the lumen is laminar under the operating conditions in this study, the local pressure drop along the lumen side at stage i can be calculated by the Hagen-Poiseulli equation [11, 41]:

$$dP_i = \frac{128\mu(\frac{L}{n})(\frac{Q_{d,avg,i}}{N})}{\pi(d_i)^4} \quad (27)$$

where μ is the kinetic viscosity of the draw solution; L is the PRO module length; $Q_{d,avg,i}$ is the average flowrate of the local draw solution at stage i , which can be determined as the average of $Q_{d,i}$ and $Q_{d,i+1}$ (Fig. 2e); n is the total number of the stages; N is the total number of hollow fibers packed in the module; d_i is the inner diameter of the hollow fiber membrane. Once the local pressure drop dP_i along the lumen side is obtained, the local pressure difference across the membrane (ΔP_i) can be determined accordingly.

The local boundary layer thickness at the draw solution side (i.e., d_s in Fig. 1) is determined by [11, 17, 32]:

$$d_s = \frac{D}{k_{lumen}} \quad (28)$$

in which D is the salt diffusivity, and k_{lumen} is the mass-transfer coefficient at the lumen side.

$$k_{lumen} = \frac{Sh_{lumen}D}{d_i} \quad (29)$$

Sh_{lumen} is the Sherwood number, which is related to the Reynolds number Re_{lumen} and the Schmidt number Sc_{lumen} . As for the laminar flow, Sh_{lumen} can be obtained by [32, 42]:

$$Sh_{lumen} = 1.62 \left(Re_{lumen} Sc_{lumen} \frac{d_i}{L} \right)^{0.33} \quad (30)$$

in which d_i is the inner diameter of the hollow fiber membrane; L is the length of the hollow fiber membrane. Re_{lumen} and Sc_{lumen} are given as below:

$$Re_{lumen} = \frac{d_i u_{lumen} \rho}{\mu} \quad (31)$$

$$Sc_{lumen} = \frac{\mu}{\rho D} \quad (32)$$

in which d_i is the inner diameter of the hollow fiber membrane; ρ and μ are the density and the kinetic viscosity of the draw solution, respectively; u_{lumen} is the velocity of the draw solution within the hollow fiber membrane, which can be determined by the local draw solution flowrate. The local boundary layer thickness at the feed side (i.e., d_f in Fig. 1) is determined using the similar method as d_s . However, an equivalent hydraulic diameter d_H is used to compute Sh_{shell} and Sc_{shell} :

$$d_H = \frac{4A_{shell}}{p_{shell}} = \frac{(d_{module})^2 - N(d_o)^2}{d_{module} + Nd_o} \quad (33)$$

where A_{shell} and p_{shell} are the cross-sectional area and the wetted perimeter of the cross-section at the shell side (i.e., the feed side), respectively; d_{module} and d_o are the inner and outer diameters of the module and hollow fiber membrane, respectively; N is the total number of hollow fibers packed in the module.

2.3.2 Algorithms

Table 1 lists all the variables and their values in the module simulation including the flowrates of the feed and draw solutions for a typical case unless otherwise stated. For a PRO module operated under the counter-current mode, as illustrated in Fig. 2, the flowrates and salinities of incoming streams (i.e., Q_d , C_d , Q_f , C_f) are known, while the flowrates and salinities of the outflowing streams from the module (i.e., Q'_d , C'_d , Q'_f , C'_f) are unknown. To enable a stage-by-stage simulation from stage one to stage n , the procedures start with guessing the Q'_f , C'_f (Fig. 2d). The proper initial values of Q'_f and C'_f can be estimated by a single stage simulation (i.e., assigning the entire module as one stage). Q'_f , C'_f and the known inputs such as Q_d , C_d serve together as the inputs to stage 1 to solve the governing equations Eq. 13 to Eq. 23. The outputs from stage 1 then work as the inputs for stage 2. Similar procedures continue until the final stage. The flowrate and salinity of the feed stream from stage n (i.e., $Q_{f,n}$ and $C_{f,n}$) can then be compared with the given Q_f and C_f . The procedures iterate until the differences between the guessed and calculated values are all less than 0.1%.

3. Results and discussion

3.1 Relationship between specific Gibbs free energy of mixing and salinities of the draw and feed solutions

The specific Gibbs free energy of mixing ΔG_V defines the maximal energy which can be harvested by mixing the feed and draw solutions to obtain 1m^3 of the mixed solution. The relationships between ΔG_V and salinities of the feed and draw solutions are given in Fig. 3. As shown in Fig. 3a, when the feed salinity is fixed at 0.011M [11, 30], ΔG_V presents a convex curve with an increase in feed mole fraction ϕ_F . In addition, the higher the draw solution salinity, the higher the ΔG_V value. ΔG_V for different draw solution salinities

approaches its peak value at about $\phi_F = 0.6$. The dependence of $(\Delta G_V)_{max}$ on the feed and draw solution salinities (represented by their molarities m_F and m_D , respectively) is presented in Fig. 3b. Obviously, $(\Delta G_V)_{max}$ obtains its maximum (point A in Fig. 3b) when there is the largest salinity difference between the feed and draw solutions.

Fig. 3c and Fig. 3d further describe the dependence of $(\Delta G_V)_{max}$ on m_F and m_D , respectively. On one hand, $(\Delta G_V)_{max}$ drops exponentially with m_F while $(\Delta G_V)_{max}$ increases relatively slowly with m_D . Moreover, a steeper $(\Delta G_V)_{max}$ decline occurs at the low m_F range, for example, 0-0.2 mol NaCl/kgH₂O. On the other hand, the draw solution is gradually diluted along the flow channels in the PRO module due to the water permeation, and the feed salinity gradually increases because of water loss and reverse salt flux across PRO membranes. However, their combined effects on ΔG_V in PRO modules may not be straightforward because the operation mode (i.e., co-current or counter-current flow) and mass transfer kinetics within the module also affect it, as elaborated in the later sections.

3.2 Mass transfer across PRO hollow fiber membranes

3.2.1 External concentration polarization effect of PRO hollow fiber membranes

External concentration polarization (ECP) effects on the feed and the draw solution sides commonly exist in all PRO operations. However, the understanding of their impacts on the performance of PRO hollow fiber membranes is still not sufficient. To elaborate on the significance of ECP effects on both sides, the profiles of water flux and power density vs. operation pressure under various boundary thicknesses are plotted in Fig. 4. It is very interesting to find that both water flux and power density decrease rapidly with an increase in the boundary thickness d_s on the draw solution side while they only slightly decrease with increasing the boundary thickness d_f on the feed side. As ECP factors on both sides have been

defined as $F_{ECP,s}$ in Eq. 14 and $F_{ECP,f}$ in Eq. 19, these two equations may provide the root causes why they response differently with an increase in boundary thickness.

As shown in Eq. 14 and Eq. 19, the ECP effect on the draw solution side is closely related to d_s and the inner radius of the hollow fiber membrane r_i , while the ECP effect on the feed side is closely associated with d_f and the outer radius of the hollow fiber membrane r_o . For the TFC hollow fiber membrane used in this study, r_i is 0.29mm, which is much smaller than r_o (i.e., 0.5mm). Therefore, the variation of d_s in Eq. 14 has a much stronger impact on $F_{ECP,s}$ than that of d_f in Eq. 19 on $F_{ECP,f}$. In other words, the asymmetric geometry of the hollow fiber membrane results in very different behaviors of water flux and power density when varying d_s and d_f .

There are two implications from the above findings. Firstly, based on Eq. 14 and Eq. 19, ECP effects on both sides can be reduced by employing hollow fiber membranes with relatively larger inner and outer diameters. However, hollow fiber membranes with a smaller diameter are sometimes preferred to provide better mechanical strength, larger surface area and higher packing density. Therefore, it is worthy of investigation in the future to design the hollow fiber membranes with the optimal inner and outer diameters for PRO applications. Secondly, as given in Eq. 28 to Eq. 33, the boundary thicknesses on both sides (i.e., d_s and d_f) are actually determined by the fluid dynamics within PRO modules. From the angle of operating PRO modules made from inner-selective membranes, more energy is needed to pump the draw solution in order to ensure a relatively larger draw solution flowrate and to reduce d_s so that the ECP effect on the draw solution side can be effectively suppressed.

3.2.2 Relationship between external performance indexes and internal factors at membrane level

To clearly understand the relationship between external performance indexes and internal factors, it is necessary to summarize all the mass transfer equations developed in the earlier section and reorganize them in the schematic system diagram in Fig. 5. This membrane level analysis will serve as the basis for the module scale investigation in later sections. As shown in Fig. 5, there are three groups of variables linking to one another in the system diagram; namely, membrane intrinsic properties, membrane structural parameters, and operational parameters. Some of the parameters can be combined to form functional factors, which play important roles in the mass transfer across the PRO membranes. These factors include ECP factors for both feed and draw solution sides, ICP factor for the porous support, and equivalent ECP or concentration polarization (CP) factors for both sides. As illustrated in Fig. 5, both the water flux and reverse salt flux are ultimately linked to the salinity gradient ΔC_m across the PRO membrane, which is determined by the surface salinities $C_{D,m}$ and $C_{F,m}$.

$C_{D,m}$ and $C_{F,m}$ actually comprise two terms with two associated factors. For example, $C_{D,m}$ consists of (1) the bulk salinity of the draw solution $C_{D,b}$ multiplied by the ECP factor on the draw solution side; and (2) the equivalent concentration J_s/J_w [30] multiplied by the equivalent ECP factor, which is due to the presence of the reverse salt flux. In addition, membrane intrinsic properties, membrane structural parameters, and operational parameters take effect at different locations in the system diagram, and result in various external performance behaviors. As investigated in the earlier section, the asymmetric nature of the hollow fiber configuration induces a significant ECP effect on the draw solution side. In fact, besides ECP factors on both sides, the hollow fiber dimensions such as r_i and r_o also impact

the ICP factor and its equivalent CP factor on the feed side. Hollow fiber membranes with different combinations of r_i and r_o are expected to display distinct J_w and PD behaviors due to the different ICP effects as well.

3.3 Module scale analysis

In a typical PRO system, PRO modules serve as the key component in the entire system. In this study, our investigation is based on a PRO module with an effective membrane area of 100m^2 . The details of the module are listed in Table 1. Various salinities and local performance indexes along the flow channels are investigated, followed by the discussion on the overall performance of the entire module. A counter-current flow is adopted as this mode is commonly accepted to be more efficient than the co-current mode [11, 12, 26].

3.3.1 Various salinities along flow channels in PRO modules

Various salinities along the flow channels within the PRO module of a typical operation case are presented in Fig. 6. As expected, $C_{F,b}$ and $C_{D,b}$ decrease with the normalized position due to the water permeation and reverse salt flux across the PRO membrane. Intermediate concentrations such as $C_{D,m}$, $C_{F,m}$ and $C_{F,t}$ follow the similar trends as $C_{D,b}$ and $C_{F,b}$ on their respective sides. In the counter-current mode, the local effective driving force for mass transfer, defined by the difference between $C_{D,m}$ and $C_{F,m}$ (or ΔC_m in Fig. 5) remains relatively stable across the length of the entire module. In addition, as enlarged in the magnified insets in Fig. 6, on the draw solution side, the significant drop from $C_{D,b}$ to $C_{D,m}$ is dominated by the dilutive ECP contribution (i.e., $C_{D,b}F_{ECP,s}$ in Eq. 15), while the J_s contribution (i.e., $\frac{J_s}{J_w}(F_{ECP,s} - 1)$ in Eq. 15 due to the presence of J_s) is negligible. Based on Eq. 15, this is because the equivalent concentration J_s/J_w ($\sim 0.007\text{-}0.008\text{M}$ in this study) caused by the presence of the reverse salt flux J_s is much smaller than $C_{D,b}$ ($\sim 0.9\text{-}1.0\text{M}$).

In contrast, the growth from $C_{F,b}$ to $C_{F,m}$ on the feed side is largely due to the ICP contribution (i.e., $C_{F,t} F_{ICP}$ in Eq. 16) and J_s contribution (i.e., $\frac{J_s}{J_w}(F_{ICP} - 1)$ in Eq. 16) inside the membrane porous support (Fig. 6b), while the ECP contribution (i.e., $C_{F,b}F_{ECP,f}$ in Eq. 17) and J_s contribution (i.e., $\frac{J_s}{J_w}(F_{ECP,f} - 1)$ in Eq. 17) outside the membrane support (Fig. 6c) are not so important. According to Eq. 16 and Eq. 17, it is because the ICP factor F_{ICP} for the membrane support (~ 4.85 - 4.99) is much larger than the ECP factor $F_{ECP,f}$ outside the membrane support (~ 1.63 - 1.66). Moreover, within the membrane porous support, the ICP contribution (i.e., $C_{F,t} F_{ICP}$ in Eq. 16) is more significant than the J_s contribution (i.e., $\frac{J_s}{J_w}(F_{ICP} - 1)$ in Eq. 16); however, the latter is still non-trivial and therefore cannot be neglected. Referring to Eq. 16, this is because the equivalent concentration J_s/J_w (~ 0.007 - 0.008 M) is now comparable to $C_{F,b}$ (~ 0.011 - 0.015 M). In summary, the dilutive ECP effect is dominant on the draw solution side, while the concentrative ICP effect is dominant on the feed side. In addition, the J_s contribution on the feed side due to the reverse salt flux is still obvious even for the TFC hollow fiber membrane having a relatively small salt permeability [30]. Further efforts in the future to develop PRO membranes with a lower salt permeability is required to suppress the negative J_s contribution toward the PRO system performance.

3.3.2 Local performance indexes along PRO modules

When a PRO module is divided into a series of stages (Fig. 2), we can use the average salinity of the incoming flow and the outgoing flow to represent $C_{D,b}$ and $C_{F,b}$ for stage i . The local performance for every stage can be calculated according to the mass transfer equations from Eq. 13 to Eq. 23. The profiles of the local performance indexes along the normalized position are displayed in Fig. 7. Here we use two pairs of indexes; namely, PD vs. PD_{max} and

SE vs. SE_{max} , to represent module scale performance. PD and PD_{max} are defined in Eq. 24 and Eq. 26, respectively. The specific energy of mixing SE harvested from a unit volume of the incoming feed and draw solutions is defined as below:

$$SE = \frac{PD \cdot A_m}{Q_f + Q_d} \quad (34)$$

in which PD , A_m , Q_f , and Q_d are referring to the power density, effective membrane area, incoming flowrates of the feed and draw solutions for every stage, respectively. SE_{max} is the maximal extractable energy obtained by mixing the feed and draw solutions. Therefore, it has the same value as the specific Gibbs free energy of mixing ΔG_V .

As shown in Fig. 7a, both the local PD and PD_{max} decline with the normalized position; however, the local PD_{max} shows a steeper decline. As power density is a product of water flux and transmembrane pressure, the decline of the local PD_{max} turns out to be a result of the reduced water flux along the module. According to Eq. 21 and Eq. 22, the water flux is proportional to the salinity gradient across the PRO membrane. As shown in Fig. 6, the gap between $C_{D,b}$ and $C_{F,b}$ decreases along the module, which is dominated by the more significant drop of $C_{D,b}$ in the draw solution side. Therefore, according to Eq. 25 and Eq. 26, the local PD_{max} shows a steeper decline along the module. In contrast, although the gap between $C_{D,m}$ and $C_{F,m}$ is also gradually reduced along the module, the decline is less significant. As a result, the ratio of PD/PD_{max} shows an upward trend in Fig. 7c. Based on their definitions given in Eq. 24 and Eq. 26, PD/PD_{max} can be considered as the mass transfer efficiency, characterizing the extent of the actual overall salinity driving force ΔC_b ($\Delta C_b = C_{D,b} - C_{F,b}$) utilized as the effective driving force ΔC_m ($\Delta C_m = C_{D,m} - C_{F,m}$) for osmotic power generation.

Fig. 8b displays the trends of the local SE and SE_{max} along the module. Instead of linking to the local mass transfer situations, the local SE and SE_{max} focus on the osmotic energy extracted from the incoming feed and draw solutions flowing through every module stage. As shown in Fig. 8b, the local SE decreases along the module. In accordance to the definition of SE given in Eq. 34, two factors contribute to the local SE reduction. On the one hand, the local SE is associated with the local PD , which is declining along the PRO module. On the other hand, with the water permeation across the membrane, both the flowrate of the draw solution Q_d and the flowrate of the feed Q_f increase along the module under the counter-current mode. Therefore, the growth of Q_d+Q_f also contributes to the declining local SE along the module. Comparing with the local SE , the local SE_{max} remains relatively stable along the entire module. Since the local SE_{max} represents the maximal extractable osmotic energy, it does not depend on the local mass transfer, but only relies on the salinities and flowrates of the incoming feed and draw solutions flowing through every module stage. Therefore, the trend of the local SE_{max} along the module can be analysed by employing the insights obtained from the relationship between the specific Gibbs free energy of mixing ΔG_V and the salinities of the feed and draw solutions (Fig. 3).

Firstly, as shown in Fig. 6, the feed salinity $C_{F,b}$ decreases with the normalized position. As indicated in Fig. 3d, a lower feed salinity promotes an enhanced local SE_{max} . However, the local SE_{max} is not only associated with the feed salinity, but also depends on the salinity of the draw solution $C_{D,b}$ as well. As shown in Fig. 6, $C_{D,b}$ actually decreases much faster than $C_{F,b}$ along the entire module. According to Fig. 3c, the declined draw solution salinity will result in a weakened local SE_{max} . Finally, since the enhancement of the local SE_{max} due to the

declining $C_{F,b}$ is effectively offset by the weakening effect resulted from the more significant drop of $C_{D,b}$, the local SE_{max} remains relatively stable along the entire module. If the PD/PD_{max} can be considered as the mass transfer efficiency, SE/SE_{max} characterizes the power harvesting efficiency describing the extent of the osmotic energy effectively harvested from the thermodynamics maximum. Combining the two trends of the local SE and SE_{max} , we can obtain the descending profile of the local SE/SE_{max} along the module (Fig. 7c). As shown in Fig. 7c, we can find that, mass transfer is enhanced along the module, while power harvesting efficiency is weakened at the same time. The strategy to address the balancing between these two aspects is the topic of the next section.

3.3.3 Module scale performance

3.3.3.1 Trade-off relationship between power density and specific energy

Enlightened by the analysis of the local performance, we begin to investigate the module scale performance such as overall PD and SE of the entire module. Module scale PD can be determined by:

$$PD = \frac{\sum_{i=1}^n PD_i A_{m,i}}{\sum_{i=1}^n A_{m,i}} \quad (35)$$

in which PD_i and $A_{m,i}$ are the local power density and effective membrane area for every stage, respectively, while n is the total stage number. Module scale SE can be determined by Eq. 34 in which PD , A_m , Q_f , and Q_d are referring to the power density, effective membrane area, incoming flowrates of the feed and draw solutions for the entire module, respectively.

To have a quick overview, the results of the module scale PD and SE under various flowrate combinations of incoming feed and draw solutions (i.e., Q_f and Q_d) are plotted in Fig. 8a by

the single-stage simulation. ECP effects on both sides are intentionally not considered temporarily. As shown in Fig. 8a, each point in the plot corresponds to a pair of PD and SE values under certain combination of Q_f and Q_d . Interestingly, there is a trade-off upper bound existing under every distinct operation pressure. In other words, an enhanced PD is always associated with a lower SE . Based on the definition of SE given in Eq. 34, an enlarged Q_f+Q_d at the denominator is required to overwhelm the enhanced PD at the numerator. This implies that PD is actually enhanced at a cost of using more feed and draw solutions; and this simultaneously lowers the SE . In addition, similarly to the trend of PD vs. the operation pressure shown in Fig. 4b and Fig. 4d, an optimal operation pressure at the module level also exists. For the operation pressure range from 5bar to 25bar, the upper bound of the PD vs. SE relationship gradually advances outwardly and stands outmost at 25bar. However, since the burst pressure of the membrane is very near to 25bar, an operation pressure of 20bar is selected for further investigations. It is also the real operation pressure used in many prior studies [11, 12, 30, 43].

To achieve an in-depth understanding of the PD vs. SE trade-off relationship, a multi-stage simulation is employed to study the typical case under the operation pressure of 20bar. All factors including the ECP effects on both sides are included during the simulation. To allow the analysis to have a universal applicability for future studies, dimensionless normalized PD and SE are used in Fig. 8b. The module scale PD is normalized by $PD_{\max}$ defined in Eq. 26, in which $C_d=1.0M$ and $C_f=0.011M$ (Fig. 2c) are used to determine $\Delta\pi_b$. The module scale SE is normalized by the maximal specific Gibbs free energy of mixing $(\Delta G_V)_{\max}$ for the salinity pair of $C_d=1.0M$ and $C_f=0.011M$, which is 0.42 kWh/m^3 (Fig. 3a). The results of the normalized PD vs. normalized SE are displayed in Fig. 8b. Although it has an upper bound contour, the trade-off relationship surprisingly consists of two patterns. The data points from

$Q_d=1\text{m}^3/\text{h}$ to $Q_d=20\text{m}^3/\text{h}$ follow a linear trade-off line with a lower slope while the data points from $Q_d=30\text{m}^3/\text{h}$ to $Q_d=100\text{m}^3/\text{h}$ form another linear trade-off line with a steeper slope.

To examine the underlying causes responsible for the slope transition between $Q_d=20\text{m}^3/\text{h}$ and $Q_d=30\text{m}^3/\text{h}$, the profiles of the boundary layer thickness in the feed side d_f vs. Q_f and the boundary layer thickness in the draw solution side d_s vs. Q_d are plotted in Fig. 8c. Evidently, both d_f and d_s profiles have a turning point when their flowrates change from $20\text{m}^3/\text{h}$ to $30\text{m}^3/\text{h}$. When Q_f and Q_d are smaller than the turning point flowrate of $20\text{m}^3/\text{h}$, d_f and d_s increase fast with a decrease in flowrate. As a consequence, ECP effects on both sides are enhanced under this condition. In contrast, when Q_f and Q_d are higher than the turning point, ECP effects on both sides are largely reduced due to the small d_f and d_s . This finding implies that the two slopes observed in trade-off lines of Fig. 8b may be due to the ECP effects within the PRO module.

To validate this assumption, Fig. 8a purposely removes the ECP effects from the simulation and check whether the PD vs. SE upper bound can be recovered to the previous pattern. Fig. 8d shows the simulation results. Consistent with our hypothesis, the normalized PD vs. SE trade-off relationship is recovered and there is only one linear upper bound. These results indicate that the ECP effect in the draw solution side still overwhelms that in the feed side. Similar to the results shown in Fig. 6 at the membrane level, the former serves as the dominant factor suppressing the module performance.

In summary, a trade-off relationship between PD and SE exists. To optimize the operation of PRO modules, firstly, a relatively higher operation pressure should be employed to enhance

both the PD and SE . More efforts to fabricate hollow fiber membranes with higher mechanical strength are important to achieve a higher operation pressure. Secondly, the PD vs. SE trade-off upper bound provides a direct guidance whether the combination of Q_f and Q_d should be further optimized. An optimal pair of Q_f and Q_d should achieve a PD and SE pair on the upper bound instead of below it. Finally, PD is actually associated with the capital expenditure (Capex) of the PRO modules. The higher the PD , the less membrane area is required for a fixed design capacity; thus the Capex can be reduced. On the other hand, SE is associated with operating expense (Opex). A higher SE implies that a smaller Q_f+Q_d is needed to achieve the fixed design capacity; therefore, Opex such as the pumping cost can be reduced. For a PRO plant design, PD and SE should be balanced in accordance to the practical considerations of Capex and Opex. In this work, a typical case consisting of $Q_d=20\text{m}^3/\text{h}$ and $Q_f=12\text{m}^3/\text{h}$ is selected for the module scale study because the performance of this pair is located near the upper bound of the trade-off line (Fig. 8b) and it has a good balance between PD and SE .

3.3.3.2 Effect of structural parameter

Besides the operation pressure and ECP effects, the membrane's structural parameter is another important factor affecting the PRO module performance. As indicated in the equation of $C_{F,m}$ in Fig. 5, the structural parameter S of hollow fibers in this study has the form of τ/φ , as suggested by Sivertsen et al. [33], in which τ is the tortuosity and φ is the porosity of the porous support. Fig. 9 shows that a reduction of structural parameter can significantly enhance water flux at both membrane and module levels because a smaller structural parameter can effectively reduce $C_{F,m}$ and enlarge the effective driving force $\Delta\pi_{eff}$ across the membrane. As a result, the water flux and power density are enhanced.

3.3.3.3 Significance of various factors on module scale performance

To understand the significance of various factors on module scale performance, the effects of these factors are compared in Fig. 10. Among all the factors, the ECP in the draw solution side and ICP in the feed side are the top two factors in determining module scale performance. To effectively mitigate the ECP effect on the draw solution side, a relatively large draw solution flowrate Q_d may be wanted to achieve high PD and SE values. On the other hand, a small structural parameter S is required to mitigate the ICP effect. In addition, as investigated in some prior works [30], ICP may also promote severe scaling within the porous support, resulting in more severe ICP and rapid water flux reduction. Therefore, more efforts are needed to find solutions in removing scaling precursors from the feed streams [11], and developing anti-scaling hollow fiber membranes [44-49].

As indicated in Fig. 10, the module performance can be also enhanced by increasing the salinity of the draw solution from 1.0M to 1.2M or by further bringing down the feed salinity from 0.011M to a fresh water level. However, although the feed salinity can possibly be reduced further, it would be more viable to explore the usage of draw solutions with higher salinities. Finally, although the membrane intrinsic properties such as the water permeability A , salt permeability B and membrane structural parameter S seem to have less significant effects on the module performance, their importance should not be neglected. In fact, since the TFC hollow fiber membrane used in this study has been well engineered to have a high A , low B and rather small S as listed in Table 1, further moderate improvements on membrane's intrinsic properties do not noticeably enhance the module performance.

4. Conclusion

This study investigates the osmotic power generation by PRO hollow fiber membranes from three perspectives; namely, thermodynamics, mass transfer across PRO membranes, and module scale simulation. On one hand, Gibbs free energy of mixing defines the upper limit of the extractable energy from the PRO process. Therefore, this concept can be used to evaluate the thermodynamics efficiency of PRO module performance. On the other hand, the mass transfer analysis at the membrane level indicates that the asymmetric nature of the hollow fiber configuration results in more significant ECP effects on the lumen side for the inner-selective hollow fiber membranes. Furthermore, a relationship framework is given to elucidate various parameters and their impacts on PRO performance. Finally, we discuss the module scale performance by first focusing on local PD vs. PD_{max} and SE vs. SE_{max} and then studying the overall module level performance. A trade-off relationship exists between the power density and the specific energy. The PD vs. SE trade-off upper bound provides a direct guidance whether the combination of the flowrates of the feed and draw solutions should be further optimized. The ECP effect in the draw solution side again plays an important role. It may change the ideal linear trade-off upper line to a two-sectional pattern. In summary, this study may not only showcase a combined approach to investigate PRO, but also provide useful insights for future PRO membrane development and operation optimization.

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Fig. 1 A schematic diagram of salt concentration across an inner-selective PRO hollow fiber membrane at steady state. Osmotic pressures corresponding to salt concentrations at different locations are illustrated in the brackets near the concentrations.

Fig. 2 A schematic diagram of the simulation approach of the PRO hollow fiber membrane module.

Fig. 3 Relationship between the specific Gibbs free energy of mixing and salinities of the feed and draw solutions.

Fig. 4 External concentration polarization (ECP) effects on the draw solution side and the feed side. d_s and d_f are the thicknesses of the boundary layer on the draw solution side and the feed side, respectively. The unit of d_s and d_f is μm . The bulk feed salinity $C_{F,b}$ and the bulk draw solution salinity $C_{D,b}$ are fixed as 0.011M and 1.0M, respectively. J_w is the water flux at the internal surface of the inner-selective hollow fiber membrane. When the boundary layer of one side changes from 0 to 100 μm , the boundary layer of the other side is set to be constant.

Fig. 5 Schematic system diagram illustrating the relationship between external performance indexes and internal factors of inner-selective hollow fiber membranes.

Fig. 6 Various salinities along the PRO module (counter-current flow, conditions of incoming streams: $Q_d=20\text{m}^3/\text{h}$, $C_d=1.0\text{M}$, $Q_f=12\text{m}^3/\text{h}$, $C_f=0.011\text{M}$, multi-stage simulation, stage number $n=100$).

Fig. 7 local PD, $PD_{\max}$; SE, $SE_{\max}$; and $PD/PD_{\max}$, $SE/SE_{\max}$ along the module.

Fig. 8 Relationship between module level specific energy SE and power density PD . (a) Upper bounds of SE vs. PD plots under various operation pressures obtained by single stage simulation without considering the ECP effects in the draw solution and the feed sides. (b) Upper bounds of normalized SE and normalized PD plots obtained by multi-stage simulation with consideration of ECP effects in both sides. (c) Relationship between the boundary layer thickness and the flowrate. (d) Upper bounds of normalized SE and normalized PD plots without considering the ECP effect in the draw solution side during simulation. The operation pressure is set at 20bar for insets (a), (b) and (c).

Fig. 9. Water flux as a function of structural parameter S ($S= \tau/\phi$) for the inner-selective membrane at the operation pressure of 20 bar. Water permeability A and salt permeability B remain unchanged. The dotted lines are the best polynomial fitting. Module level results are obtained from a typical case with $Q_d=20\text{m}^3/\text{h}$, $C_d=1.0\text{M}$, $Q_f=12\text{m}^3/\text{h}$ and $C_f=0.011\text{M}$. Membrane level results are obtained from the case with very large flow rates ($Q_d=100\text{m}^3/\text{h}$ and

$Q_f=100\text{m}^3/\text{h}$), in which the bulk concentrations of the draw solution and the feed along the entire module actually remains constant ($C_{D,b}=1.0\text{M}$ and $C_{F,b}=0.011\text{M}$).

Fig. 10. Factor analyses of module level performance for the typical case with $Q_d=20\text{m}^3/\text{h}$, $C_d=1.0\text{M}$, $Q_f=12\text{m}^3/\text{h}$, $C_f=0.011\text{M}$ and the operation pressure is set at 20bar.

Table 1 Membrane parameters and module dimensions for simulation

Variable	Value
1. Membrane model parameters	
Water permeability, A [LMH/bar]	3.5
Salt permeability, B [LMH]	0.3
Membrane structural parameter, τ/φ [-] ^a	2.8
Temperature, T [K]	298
Diffusion coefficient for NaCl (m^2/s)	$1.61\text{E}-9$
Draw solution concentration, $C_{D,b}$ [mol/L]	1.0
Feed water concentration, $C_{F,b}$ [mol/L]	0.011
Outer radius of fibre, r_o [mm]	0.50
Inner radius of fibre, r_i [mm]	0.29
2. Module parameters	
The draw solution inlet flow rate, Q_s [m^3/h]	20
The feed solution inlet flow, Q_f [m^3/h]	12
TMP at the sea water brine inlet, ΔP [bar]	20
The hollow fibre length, L [m]	2
Total number of hollow fibers, N [-]	27437
The module inner diameter, d_{module} [inch]	12
The module effective membrane area, A_m [m^2]	100
Number of stages, n [-]	100

^a The value is obtained by data fitting of the performance of small PRO modules

Highlights

- A comprehensive analysis of fluid motion, mass transport, thermodynamics and power generation during PRO processes was conducted.
- A state-of-the-art inner-selective TFC hollow fiber membrane was employed in the modelling.
- The asymmetric nature of hollow fibers results in more significant external concentration polarization in the lumen side of the inner-selective hollow fiber membranes.
- A trade-off relationship exists between the power density (PD) and the specific energy (SE).
- The PD vs. SE trade-off upper bound provides a useful guidance to optimize PRO module operation conditions.

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