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Osmotic power generation by inner selective hollow fiber membranes: An investigation of thermodynamics, mass transfer, and module scale modelling

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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.

1. 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

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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_2O)
m_D	molality of NaCl in the draw solution (mol/kg-H_2O)
m_F	molality of NaCl in the feed solution (mol/kg-H_2O)
$m_\pm$	mean ionic molality of the salt (mol/kg- H_2O)
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/m2)
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 fibers (m)
r_o	outer radius of hollow fibers (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 (γ=2 for NaCl)
$\gamma_\pm$	mean ionic activity coefficient based on $m_\pm$ (-)
π	osmotic pressure (bar)
Δπ	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)
lumen	lumen side of hollow fibers (i.e., draw solution side)
shell	shell side of hollow fibers (i.e., feed solution side)

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