Chemical Engineering Journal 249 (2014) 236–245

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Thin film composite forward-osmosis membranes with enhanced internal osmotic pressure for internal concentration polarization reduction

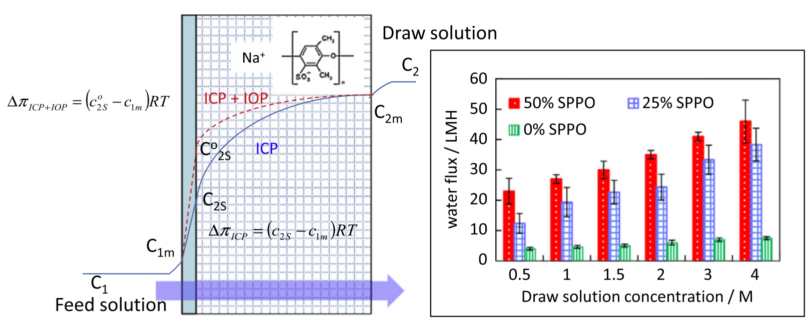
Zhengzhong Zhou, Jim Yang Lee *, Tai-Shung Chung

Department of Chemical & Biomolecular Engineering, National University of Singapore 10 Kent Ridge Crescent, Singapore 119260, Singapore

HIGHLIGHTS

- FO membranes were prepared by incorporating SPPO in substrate.
- IOP was generated in the SPPO/PSf membranes.
- The effects of IOP were demonstrated via structural parameter analysis.
- ICP was mitigated in the SPPO/PSf membranes.
- High water fluxes were demonstrated in FO seawater desalination.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 January 2014
Received in revised form 6 March 2014
Accepted 13 March 2014
Available online 24 March 2014

Keywords:
Forward osmosis
Sulfonated polymeric membrane
Desalination
Water purification
Concentration polarization

ABSTRACT

Thin-film composite (TFC) forward-osmosis (FO) membranes with enhanced internal osmotic pressure (IOP) were used to reduce internal concentration polarization in this study. These TFC membranes contained a selective polyamide layer deposited by interfacial polymerization on a support substrate cast from a polymer blend of polysulfone (PSf) and sulfonated poly(phenylene oxide) (SPPO). The immobilized counter ions (Na^+) in SPPO gave rise to an IOP which facilitated water transport in the AL–FS operating mode (i.e., the active layer is facing the feed solution, also referred to as the FO mode) but retarded water transport in the AL–DS operating mode (i.e., the active layer is facing the draw solution, also called as the pressure retarded osmosis (PRO) mode). An optimized TFC membrane could draw a water flux of 39 LMH ($Lm^{-2}\,h^{-1}$) in the AL–FS mode, which is among the highest in the current literature; and 57 LMH in the AL–DS mode, which is comparable to other published works using deionized water as the feed and 2 M NaCl as the draw solution. The optimized SPPO/PSf TFC membrane also outperformed other published FO membranes in simulated seawater desalination. Extremely high water fluxes of 25 and 19 LMH could be obtained in the AL–DS and AL–FS modes respectively. The impressive high water flux in the AL–FS mode makes this membrane particularly suitable for FO operations where internal concentration polarization (ICP) and membrane fouling are major concerns.

1. Introduction

Forward osmosis (FO), an osmotic driven membrane process which harvests fresh water from seawater, brackish and municipal wastewater, is a potential technological solution to global water shortage where more than 1.2 billion people have no access to clean water [1–6]. In FO desalination, seawater and a concentrated draw solution are separated by a semi-permeable membrane (the FO membrane); the osmotic pressure difference between the two solutions drives water flow from the seawater to the draw solution across the membrane without any externally applied pressure;

* Corresponding author. Fax: +65 67791936.
E-mail address: cheleejy@nus.edu.sg (J.Y. Lee).

http://dx.doi.org/10.1016/j.cej.2014.03.049
1385-8947/

Nomenclature

Abbreviations

AL–DS	active layer facing the draw solution
AL–FS	active layer facing the feed solution
DI	de-ionized
ECP	external concentration polarization
FO	forward osmosis
ICP	internal concentration polarization
IEC	ion exchange capacity
IOP	internal osmotic pressure
IP	interfacial polymerization
MPD	M-phenylene diamine
PSf	polysulfone
RO	reverse osmosis
SPPO	sulfonated poly(phenylene oxide)
TFC	thin-film composite
TMC	trimesoyl chloride

Symbols

A	water permeability coefficient
A_m	membrane area
B	salt permeability coefficient
C	concentration
D	salt diffusivity
d_h	hydraulic diameter of FO cell channel
ΔF	free energy of mixing
f	number of ions per chain
J_v	water flux
J_s	salt flux
k	mass transfer coefficient
k_B	Boltzman constant
L	length of FO cell channel
l	membrane thickness
m	mass
N	Avogadro's number
P	hydraulic pressure
R	gas constant
R_s	salt rejection
Re	Reynolds number
S	structural parameter
Sc	Schmidt number
Sh	Sherwood number
T	temperature
t	time
x	number of chains per unit volume
V	volume
ε	membrane porosity
π	osmotic pressure
τ	membrane tortuosity
ρ	density
υ	molar volume of solvent
φ	volume fraction of polymer network

the draw solute is then regenerated with the concurrent production of pure water. In comparison with other desalination processes such as reverse osmosis [7–10], membrane distillation [11], capacitive deionization [12] and electrodialysis [13] where high hydraulic pressure, high temperature or electrical energy is needed, FO processes have some notable advantages: no energy input is required to transport water across the membrane in the FO unit, and draw solute regeneration may make use of renewable energy or low grade waste heat if thermo-responsive or photon-responsive draw solutes [2–4,14] are used. One scenario involves the precipitation of the draw solute after moderate heating, lowering the osmotic pressure of the draw solution and hence the hydraulic pressure required in a subsequent filtration process [15]. In addition, membrane fouling in FO can also be managed more easily than in RO [16–18] to result in the reduction of the operating cost. All of these considerations could lead an overall smaller environmental footprint.

Apart from the design of novel draw solutes which is essential to the economic viability of FO desalination, the FO membrane design should also be improved to enable process intensification based on productivity (a high water flux) and quality (a low salt leakage rate). One critical issue in FO processes is the diminution of water flux by internal concentration polarization (ICP) [19–21]. ICP is caused by the membrane resistance to diffusion, resulting in a serious dilution of the draw solution in the AL–FS mode or a slight increase in the feed concentration in the AL–DS mode. Consequently, the osmotic pressure difference across the membrane active layer is reduced, as shown in Fig. 1 (solid curves). Unlike external concentration polarization (ECP) which occurs outside the membrane, ICP resides inside the porous support and as such cannot be mitigated by increasing the water flow rate or turbulence. FO membranes have to be designed differently from the RO membranes with ICP mitigation as the key consideration. Recent studies on TFC FO membranes have made notable progress in meeting the FO requirements [22–27]. An important feature of the TFC membranes is independent tailorability of the selective and support layers to meet different application demands. For a prospective TFC-FO membrane, the TFC layer, formed by the interfacial polymerization (IP) of an amine and a carboxylic acid or acid chloride, should be designed for high solute rejection and low water resistance by optimizing the IP conditions [28], the substrate surface chemistry [22,29] and post-synthesis treatments [30]. The substrate, formed via phase inversion, should be thin and porous for ICP reduction, and yet has sufficient mechanical, chemical and thermal stability to withstand industrial operations. Research over the years has shown that hydrophilic substrates such as sulfonated polysulfone [31], sulfonated poly (ether ketone) [30] and sPES-co-sPPSf (sulfonated polyethersulfone and polyphenylsulfone copolymer) [23,32] are more capable of high water flux. Substrate hydrophilicity aside, a factor that has previously been overlooked is the effect of cations (e.g. Na^+) associated with the sulfonated material in the membrane. In an early study on polymer gel swelling, Flory equated the swelling pressure to the net osmotic pressure of the polymer gel [33], which Amiya and Tanaka described as IOP [34]. IOP is significantly higher in ionic than non-ionic polymer networks as a result of charge localization [33] and the translational degree of freedom of counterions [34] in a polymer network. Hence IOP is likely to be universal in polymeric membranes containing ionizable groups. In osmotic pressure membrane processes such as FO, however, the effect of IOP has thus far not been included in the analysis of the FO performance. If the substrate of an FO-TFC membrane contains an ion-exchange polymer, IOP can be generated by the counterions immobilized in the substrate, which increases the effective driving force in the AL–FS mode and decreases the effective driving force in the AL–DS mode (the dotted curves in Fig. 1); resulting in a higher water flux for the former and a lower water flux for the latter. It should be mentioned that the AL–FS mode is the preferred operating mode for desalination because feed water foulants are deposited on the TFC layer; and are much easier to remove than