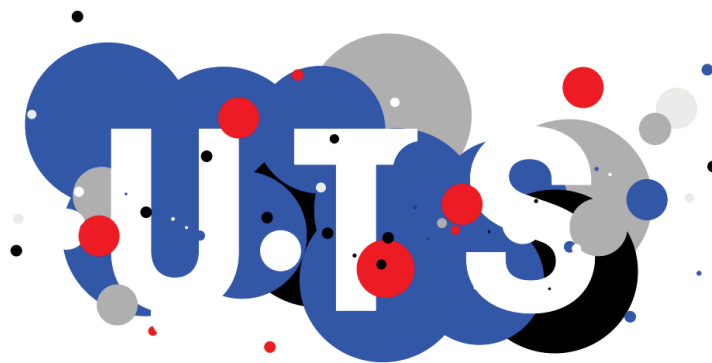


**DEVELOPMENT OF THIN FILM
COMPOSITE MEMBRANES FOR
OSMOTICALLY DRIVEN MEMBRANE
PROCESSES**

by

Myoung Jun Park

A Thesis submitted in fulfilment for the degree of
Doctoral of Philosophy



**School of Civil and Environmental Engineering
Faculty of Engineering and Information Technology
University of Technology Sydney (UTS),
New South Wales, Australia**

October 2018

CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of candidate

Myoung Jun Park

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LIST OF ABBREVIATIONS

APTMS	Aminopropyltrimethoxy silane
FTIR	Fourier transform infrared spectroscopy
BDSA	Benzidinedisulfonic acid
BTEC	Biphenyl tetra-acyl chloride
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAIP	Co-solvent assisted IP
CAP	Cellulose acetate propionate
CECP	Cake-enhanced concentration polarization
CNTs	carbon nanotubes
CP	Concentration polarization
CTA	Cellulose triacetate
DAT	Diaminotoluene
DFBP	Difluorobenzophenone
DI	Deionised
DI water	Deionized water
DMAc	<i>N,N</i> -Dimethylacetamide
DMAPS	Dimethyl-(3-sulfopropyl)ammonium hydroxide
DMSO	Dimethyl sulfone
DS	Draw solution
ECP	External concentration polarisation
ED	Electrodialysis
FE-SEM	field emission scanning electron microscope
FO	Forward osmosis
FS	Feed solution
GO	Graphene oxide
GOTMS	3-glycidyloxypropyltrimethoxysilane
HF	Hollow fiber
HTI	Hydration technology innovations
ICP	Internal concentration polarisation
ID	Inner diameter
IP	Interfacial polymerization
IPC	Isophthaloyl chloride
LbL	Layer-by-layer
MEL	Metacryloyloxyethyl lipoate
MF	Microfiltration
MOF	Metal-organic frameworks
MPC	methacryloyloxyethyl phosphorylcholine
MPD	<i>m</i> -phenylenediamine
MW	Molecular weight
NIPS	Non-solvent induced phase separation
OD	Outer diameter
PA	Polyamide
PAA	Polyacrylic acid
PAI	Polyamide-imide
PAN	Polyacrylonitrile

PAO	Pressure assisted osmosis
PBI	Polybenzimidazole
Pei	Polyetherimide
PEI	Polyethyleneimine
Pei	Polyetherimide
PES	Polyethersulfone
PET	Polyethylene terephthalate
PIP	Piperazine
POSS	Polyhedral oligomeric silsesquioxane
PPD	<i>p</i> -phenylenediamine
PPO	Poly(phenylene oxide)
PPSU	polyphenylsulfone
PRO	Pressure retarded osmosis
PSf	Polysulfone
PSS	Polystyrene sulfonate sodium
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
PVP	polyvinylpyrrolidone
rGO	Reduced graphene oxide
RO	Reverse osmosis
RSF	Reverse solute flux
sDCDPS	3,3'-di-sodiumdisulfate-4,4'-dichlorophenyl sulfone
SDS	Sodium dodecyl sulfate
SPEK	Sulfonated poly(ether ketone)
sPPSU	Sulfonated polyphenylenesulfone
SRSF	Specific reverse solute flux
TEOS	Tetraethylorthosilicate
TFC	Thin-film composite
TFN	thin film nanocomposite
TMC	Trimesoyl chloride
TPC	Terephthaloyl chloride
UF	Ultrafiltration
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

A	Pure water permeability coefficient ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ or LMH/bar)
B	Salt permeability coefficient (ms^{-1})
C	Molar solute concentration (Moles or M)
D	Solute diffusivity ($\text{m}^2 \text{s}^{-1}$)
d_h	Hydraulic diameter (m)
J_s	Reverse salt flux ($\text{g m}^{-2} \text{h}^{-1}$ or $\text{mmoles m}^{-2} \text{h}^{-1}$ or gMH)
J_v or J_w	Water flux ($\text{L m}^{-2} \text{h}^{-1}$ or LMH)
k	Mass transfer coefficient
K	Solute resistivity (sm^{-1})
L	Length of channel (m)
M	Molar concentration of the solution (Moles or M)
M_w	Molecular weight (Mole/g)
P	Applied pressure (bar)
Re	Reynolds number
R	Salt rejection (%)
Sc	Schmidt number
Sh	Sherwood number
π	Osmotic pressure (bar)
S	Structural parameter (M)
X_A	Mole fraction of the solvent (Moles or M)
$\Delta\mu^*_A$	Chemical potential of the pure solvent
$\Delta\mu_A$	Chemical potential of the solvent in solution
n	Amount of solute molecules
V_m	Volume of the solvent (L or ml)
T	Temperature ($^{\circ}\text{C}$)
n	Amount of solute molecules
R	Ideal gas constant ($\text{L atm mol}^{-1} \text{K}^{-1}$)
i	Van't Hoff factor
C_s	Solute concentration (Moles or M)
R_s	Salt rejection coefficient (%)
C_f	Feed solute concentrations (Moles or M)
C_d	Draw solute concentrations (Moles or M)
x or t_s	Thickness (m)
τ	Tortuosity
ϕ or ε	Porosity
σ	Reflection coefficient
S_m	Effective membrane surface area
$\pi_{D,b}$	Osmotic pressures of the bulk draw solution (bar)
$\pi_{F,m}$	Osmotic pressures of the bulk feed solution (bar)
R_a	Mean roughness (μm)
R_{ms}	Root mean square of z values (μm)
R_{max}	Maximum vertical distance between the highest data points (μm)
d_p	Solute diameter (m)
μ_p	Mean effective pore size (nm)
σ_p	Geometric standard deviation

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ABSTRACT

Rapid population growth and continuous economic development have resulted in a significant increase in the demand and accessibility of clean water energy resources. To solve these issues, osmotically driven processes including forward osmosis (FO) and pressure retarded osmosis (PRO) are hold some of the greatest potential in providing sustainable solutions for the global needs of both clean water and clean energy. Basically, both FO and PRO processes utilize feed solution (FS) with low salt concentration and draw solution (DS) with high salt concentration, which can drive the high osmotic pressure difference through the semi-permeable membrane to extract clean water and to produce clean energy. However, due to the poor membrane performances of commercially available membranes, properly designed high performance FO and PRO membranes need to be developed for viable applications.

Polymeric membranes for FO and PRO processes can be fabricated through a variety of methods, which include phase inversion, electrospinning, and hollow fiber spinning. FO and PRO membranes are typically made of a thin film composite (TFC). TFC membranes have a porous membrane support layer which facilitates convenient water transport while a thin active layer (i.e. polyamide) is responsible for high salt rejection. Due to their higher water permeability and lower reverse solute permeability as compared to the commercial cellulose triacetate (CTA, Hydration Technology Innovations, Inc. USA), in this study, development of high performance TFC membranes have been subjected to modifying membrane support layers using various fabrication techniques and approaches including physical and chemical modifications.

TFC-FO and -PRO membranes were newly designed and fabricated by incorporating hydrophilic graphene oxide (GO) nanomaterials into membrane support layer for improved membrane performance. In the case of TFC-FO membrane development, different amounts of GO nanosheets were incorporated in the polysulfone (PSf) to obtain PSf/GO composite flat-sheet membrane supports via a phase separation technique. Results reveal that at an optimal amount of GO addition, a PSf/GO composite support layer with favourable structural property measured in terms of thickness, porosity and pore size can be achieved due to the effect of hydrophilic GO. The optimum incorporation of GO in the PSf support layer not only significantly improved water permeability but

also allowed effective polyamide (PA) layer formation, by comparison to that of a pure PSf support layer which had much lower water permeability. Thus, a TFC-FO membrane with high water flux (19.77 LMH against 6.08 LMH for pure PSf) and reverse flux selectivity (5.75 Lg^{-1} against 3.36 Lg^{-1} for pure PSf) was obtained under the active layer facing the feed solution (AL-FS). Besides the improved structural properties (reduced structural parameter, S) of the support layer, enhanced support hydrophilicity also contributed to the improved water permeability of the membrane. Therefore, the GO modification of membrane supports for TFC-FO membranes showed a promising technique to improve the FO performance.

With the similar concept and perspectives of the GO effect on FO membrane performance, TFC-PRO hollow fiber membranes were also fabricated with incorporating GO into the hollow fiber membrane supports via a hollow fiber spinning device. Polyethersulfone (PES) was selected as membrane material due to its good chemical resistance, high mechanical properties, and easy in membrane fabrication. The hollow fiber membrane, fabricated by incorporation with small amounts of GO into the PES support layer, revealed the improvement in membrane porosity, hydrophilicity and pure water permeability without compromising mechanical properties when compared to the pure PES support layer. Therefore, the TFC hollow fiber PES/GO membrane showed significantly high PRO flux while maintaining the low reverse salt flux (RSF) at higher hydraulic pressures, resulting in high power density of 14.6 W m^{-2} at the highest applied pressure of 16.5 bar. Experimental results showed that optimum concentration of GO can be adapted as a filler of hollow fiber membranes for the TFC-PRO membrane for enhancing PRO performance without hampering its mechanical properties.

Fabrication of electrospun nanofiber support membranes for TFC-FO membrane via the electrospinning technique have drawn attention in recent years due to their high porosity, interconnected pore structure, high strength to weight ratio, low tortuosity, and ease in controlling membrane thickness (deposition time by electrospinning). Therefore, a novel electrospun nanofiber support for a high performance TFC-FO membrane was fabricated via coaxial electrospinning. This method produces a dual layer core/sheath polyvinylidene fluoride (PVDF)/cellulose acetate (CA) composite nanofiber support, prior to interfacial polymerization (IP) to produce the selective PA layer. The electrospun

nanofiber support was expected to exhibit hydrophilicity at the sheath side due to CA, and mechanical stability at the core side due to PVDF, both of which properties are preferred for TFC-FO membranes. The physical and morphological properties of composite TFC-FO membranes were characterized and the membrane performance was evaluated during FO tests, and compared with single CA, single PVDF and blend (CA/PVDF) nanofiber membranes. The composite CA/PVDF support prepared via coaxial electrospinning showed marked significant improvement in hydrophilicity due to the presence of CA on the sheath side of nanofibers, while PVDF at the core side of nanofibers retained the mechanical strength comparable to the pure PVDF nanofiber support. In the FO test result using 0.5 M NaCl as a draw solution and DI water as a feed solution, the composite CA/PVDF TFC-FO membrane achieved high FO flux (31.2 LMH) and remarkably low specific reverse salt flux (*SRSF*, 0.03 g/L) with a low structural parameter (190 μm).

In spite of many advantageous characteristics of nanofiber supports for an FO membrane, there is a membrane swelling issue with nanofiber support fabricated by hydrophilic polymers which weaken the mechanical properties since they are wetted in liquids. In addition, although it was found that the FO performance improved with composite CA/PVDF nanofiber substrate, overall mechanical properties of FO membrane supports which, when prepared by electrospinning, still seem to be one of the major obstacles for practical applications. To overcome these issues, mechanically stable hydrophobic PVDF nanofiber support was treated by heat press near the melting point (170°C) of PVDF and then hydrophilic polyvinyl alcohol (PVA) was utilized to improve the hydrophilicity as well as mechanical strength for TFC-FO membranes. The PVDF nanofiber support was modified with PVA via dip coating and acid-catalyzed crosslinking with glutaraldehyde (GA) prior to the formation of the PA active layer on the support via IP. The influence of PVA modification on the morphology and physical properties of PVDF support was evaluated through several characterization techniques while the flux performance was assessed using a lab-scale FO membrane unit. The fabricated PVA-modified TFC FO membranes exhibited high hydrophilicity, porosity, and mechanical strength, therefore resulting in excellent FO performance (24.8 LMH using 0.5 M NaCl and DI water as draw and feed solution, respectively). Dip coating of the nanofiber support in PVA is therefore a simple and effective method for the improvement of PVDF support with high

mechanical properties as well as hydrophilicity to fabricate high performance TFC FO membranes.

In this study, high performance engineered osmosis membranes were successfully developed through the membrane substrate modifications either by GO incorporation or hydrophilic surface modifications. Membrane substrates incorporated with small loadings of GO (≤ 0.25 wt%) exhibited significantly improved membrane performance for both FO and PRO applications via enhanced hydrophilicity and membrane porosity without deterioration of mechanical properties. For further improvement of FO flux, porous and a low tortuous electrospun nanofiber supports were used as FO membrane supports and additionally modified the nanofibers via coaxial electrospinning or hydrophilic PVA dip-coating for having both hydrophilic and mechanically stable properties. Therefore, a hydrophilic modification of membrane substrates without consideration of type of substrates for engineered osmosis has high potential to improve the membrane performance.