**Thin Films** 



Water Transport through Ultrathin Polyamide Nanofilms Used for Reverse Osmosis

Zhiwei Jiang, Santanu Karan, and Andrew G. Livingston\*

Barrer Center, Department of Chemical Engineering Imperial College London, South Kensington Campus, Exhibition Road, London SW7 2AZ, UK; Membrane Science and Separation Technology Division, CSIR-Central Salt and Marine Chemicals Research Institute, GB Marg, Bhavnagar 364002, Gujarat, India.



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Support membranes

Nanofilm composite membranes

#### What is Reverse Osmosis (RO)?

- ✓ Reverse Osmosis is a process by which a solvent passes through a porous membrane in the direction opposite to that for natural osmosis when subjected to a hydrostatic pressure greater than the osmotic pressure.
- ✓ The Reverse Osmosis is a process where molecules are forced through a semi-permeable membrane to form a less concentrated solution. Essentially, the membrane acts like a type of filter as it has extremely tiny pores that help remove microscopic contaminants from the water you drink by straining them out.
- ✓ Osmosis is defined as the process of molecules passing through a semi-permeable membrane from a less-concentrated solution into a more-concentrated solution. *Reverse* osmosis is simply the opposite of that process.



## Why I have chosen this paper?

- Currently, more than 300 million people around the world rely on desalinated water for part or all of their daily needs. That demand will only grow with larger populations and improved standards of living around the world.
- Accessing the oceans for drinking water, however, requires desalination technologies that are complicated and expensive. The most commonly used technology for desalination is reverse osmosis (RO), a process in which seawater is forced through a membrane capable of removing salts and other small molecule contaminants. While the use of RO continues to rise around the world, many of its drawbacks, which include high energy consumption and a propensity for membranes to foul, continue to plague the industry.
- New approach to membrane production that makes us rethink how to design and use RO membranes for desalination. This paper shows a simple process for making thin polyamide nanofilms at a free aqueous-organic interface and it's showing good water rejection capacity of the membrane.

## What is this work about

In this paper they have discussed about a simple technique to prepare thin polyamide nanofilms for RO membrane and its performances on different polymeric supports were shown.

## **Relevance to the group or my work**

This paper shows how easily thin polyamide nanofilms can be made. So, whoever working on different type of membrane, they can use this technique to prepare the membrane.

# **BRIEF INTRODUCTION**



# **INTERFACIAL POLYMERIZATION**



Schematic representation of chemical interactions between MPD and TMC relevant to membrane formation by interfacial polymerization.

## In this paper....

- The most commonly used technology for desalination is reverse osmosis (RO), a process in which seawater is forced through a membrane capable of removing salts and other small molecule contaminants.
- The challenging task to create ultra-thin, ultra-smooth polyamide membranes that are less prone to fouling and may require less power to move water through them.
- To reduce the area requirement, increased membrane permeance (liter per hour per sq. meter per bar; permeability/thickness) is sought, where permeability of the separating layer, as a material property, is assumed to be constant.
- Therefore, reduction of the separating layer thickness is an evident strategy for enhancing the membrane permeance by providing shorter distances for liquid transport.
- Thin-film composite membranes used for desalination by reverse osmosis (RO) are made via interfacial polymerization (IP) on a porous support, producing a crumpled polyamide separating layer ~50 to 200 nm.
- Due to the complex morphology of this polyamide separating layer, reducing its thickness has not yet been reported as an approach to increasing water permeance in RO membranes.
- ➤ In this paper, they were able to vary the morphology of the separating layer from smooth to crumpled, where the crumpled features resulted from the folding and stacking of nanofilms, and so had the same intrinsic wall thicknesses as the smooth nanofilms of ≈8 nm.

## **Results and discussion**

## Fabrication of polyamide nanofilms



Schematic of free-standing polyamide nanofilms fabricated at a free interface. a) Instantaneous formation of polyamide nanofilm at the interface between an aqueous phase containing MPD and a hexane phase containing TMC. b) Free-standing polyamide nanofilms were picked-up by a substrate. c) Polyamide nanofilms with diameter ~10 cm and thickness varying from ~6 to 15 nm were lifted out of the biphasic mixture. d) Nanofilms were floated off the substrate onto a water surface. e) Defect-free nanofilms were allowed to extend on the water surface. f) Nanofilms were transferred onto the supports. g) A nanofilm composite membrane with the polyamide nanofilm as the active layer on the support.



#### Support membranes

Nanofilm composite membranes

Schematic of the interfacial polymerization process at a free aqueous–organic interface (IP@FI) and the subsequent fabrication of nanofilm composite membranes. a) Fabrication of an ultrathin polyamide nanofilm at a free aqueous– organic interface between an aqueous phase containing m-phenylenediamine and a hexane phase containing trimesoyl chloride. The front surface faces the hexane phase and the rear surface faces the aqueous phase. The growth of the nanofilm was terminated by picking it up from the interface with a polycarbonate substrate pre-submerged in the aqueous phase, and refloating it onto a fresh water surface. b) Nanofilm composite membranes were fabricated by reattaching the polyamide nanofilms on various support membranes including crosslinked polyimide, crosslinked polyetherimide, polysulfone, and hydrophilic polytetrafluoroethylene.



Optical and microscopic images of polyamide nanofilms fabricated at the free aqueous–organic interface. a) Photographic image of an  $\approx 10$  nm thick nanofilm covering a diameter of  $\approx 10$  cm transferred from the interface and refloated on a water surface, where a ruler was immersed in the water underneath the nanofilm. b) SEM image of a polyamide thin-film composite membrane fabricated using a polysulfone support via conventional interfacial polymerization at a supported interface using 2 wt% MPD and 0.1 wt% TMC reacted for 1 min (IP-2%-0.1%-Psf). c) SEM image of a polyamide nanofilm fabricated with identical conditions as for panel (b) at a free interface (IP@FI-2%-0.1%) and then transferred onto a polysulfone support. The effect of the two modes of interfacial polymerization on the resulting surface morphology of the nanofilms is clear in the contrast between panels (b) and (c). d,e) SEM images of the front surface (facing the hexane phase) and the rear surface (facing the aqueous phase) of the nanofilm made from 3 wt% MPD and 0.15 wt% TMC reacted for 1 min (IP@FI-3%-0.15%), and transferred onto polysulfone supports. f) SEM cross-sectional image of a free-standing nanofilm (IP@FI-3%-0.15%) with nodular features as observed on the surface (d). g,h) AFM height image and profile of a free-standing nanofilm transferred onto a silicon wafer. The nanofilm was prepared from 0.05 wt% MPD and 0.025 wt% TMC reacted for 1 min at a free interface (IP@FI-0.05%-0.025%). A scratch was made to expose the silicon wafer surface for the measurement of nanofilm thickness. i) SEM images of a free-standing nanofilm (IP@FI-0.05%-0.025%) transferred onto a PTFE support. Inset shows an image at a higher magnification, for which the arrow indicates the edge of the nanofilm.



Surface and cross-sectional SEM images of support membranes. a and b) XP84 supports. c and d) XPEI supports. e and f) Polysulfone supports. g and h) Hydrophilic PTFE supports.



Properties of free-standing polyamide nanofilms fabricated at a free aqueous–organic interface. a) XPS survey spectra of the nanofilms under two different concentrations of MPD and TMC. Free-standing nanofilms were transferred onto gold (Au)-coated silicon wafers. b) Plot of (i) the Au concentrations (at%) detected from the substrate as measured with XPS and (ii) nanofilm thickness as measured from AFM height profiles with varying MPD concentration in the interfacial polymerization reaction. c,d) XPS narrow scan spectra of C1s measured from the front and rear surfaces of the nanofilms and the deconvoluted spectra for the probable chemical species. Nanofilms were prepared with 3 wt% MPD and 0.15 wt% TMC reacted for 1 min (IP@FI-3%-0.15%). e)  $\zeta$  potential curves for the front and rear surfaces of the nanofilm (IP@FI-3%-0.15%). f) Variation of mass per unit area of the nanofilms measured with a quartz crystal microbalance under dry, 94% relative humidity, and immersion (in water) environments with increasing nanofilm thickness. The mass uptake (g water g-1 dry nanofilm) was calculated from the increase in mass under saturated water vapour (94% RH) conditions or increase in mass upon immersion into water.



Reverse osmosis desalination performance of nanofilm composite membranes. a) Variation of permeance and salt (NaCl) rejection over time for nanofilm composite membranes. Nanofilms were prepared with 3 wt% MPD and 0.15 wt% TMC reacted for 1 min at the free aqueous– organic interface (IP@FI-3%-0.15%) and then attached onto a polysulfone support with either front or rear surfaces facing the feed (NaCl) solution. b) Plot of the water permeance and salt (NaCl) rejection of nanofilm composite membranes versus the pure water permeance of support membranes. All nanofilms (IP@FI-3%-0.15%) were fabricated under identical conditions and subsequently transferred onto different supports. c) Variation of water permeance and permeability of nanofilm composite membranes attached onto a polysulfone support versus the nanofilm thickness. All reverse osmosis experiments were conducted in a crossflow rig at 30 °C and 100 L h–1 crossflow velocity (two parallel rows of membrane cells at 50 L h–1) under 20 bar with 2 g L–1 NaCl feed solution. The error bars represent the standard deviation calculated from the performance measurement of at least three independent samples. L m–2 h–1 bar–1 stands for liter per square meter per hour per bar.



Performance of composite membranes comprising ~6.5 nm nanofilms on polysulfone supports at different operating conditions. a) increasing crossflow velocities per row of membrane cells and b) increasing applied pressures. All data in a) were collected in a crossflow rig under 15.5 bar with 2 g.L-1 NaCl feed solution at a recovery of 15%. All data in b) were collected in a crossflow rig with 50 L/h per row of membrane cells with 2 g/L. NaCl feed solution at a recovery of 15%.

## Conclusion

- ✤ In this paper, they report smooth polyamide nanofilms fabricated at a free aqueous organic interface and used to form nanofilm composite membranes for desalination.
- ✤ This approach enables the control of nanofilm thickness from ≈6 to 15 nm, and the nanofilms exhibit a nonlinear increase in permeability as the thickness reduces below 8 nm.
- ★ These sub-8 nm nanofilms transferred onto the ≈200 nm pore size PTFE supports (IP@FI-0.05%-0.025%-PTFE) were sufficiently rigid to withstand pressurization at 20 bar, and exhibited a water permeance of ~4.06 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> with NaCl rejection of ~93.3 %
- Composite membranes comprising sub-8 nm nanofilms show similar performance to commercial membranes with crumpled surface morphologies. This study suggest that both nanofilm thickness and support permeance could be engineered to create RO membranes with significantly higher permeance, and comparable rejection, to those employed in industry.

# **MODIFICATION OF TFC MEMBRANE**



Schematic representation of chemical interactions between polyamide cross-linked layer with GO.

Ali M. et al., Desalination **2016**, 386, 67–76.

