

Energy Generation from Osmotic Pressure Difference Between the Low and High Salinity Water by Pressure Retarded Osmosis

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Abstract: Osmosis is a natural phenomenon and exists widely from the salinity gradient between sea water and fresh water. This green energy can be captured using pressure retarded osmosis (PRO). A potential energy of 2.5 terawatts is available globally from rivers flowing into the sea. Membrane is the key component and it has been the main limitation for this technique. The most challenging problem is the internal concentration polarization (ICP) which reduces the water flux by up to 80 %. This paper reviews most critical and recent publications on membrane fabrication (e.g. composite membrane, hollow fiber membrane). Summary and perspectives will be given in order to prepare high performance membranes.

Keywords: Osmosis, pressure retarded osmosis, membrane, concentration polarization.

INTRODUCTION

With the growing population and life expectation, energy demand is predicted to increase rapidly in the future. Currently, the energy production from fossil fuels is predominant and it raises a lot of severer issues such as global warming and environmental pollutions. Developing sustainable energy techniques is the only solution to maintain the long-term prosperity of our society. In 1954, the concept of harvesting electric power from mixing fresh and salt water was proposed by Pattle for the first time [1]. A maximum energy of 0.8 kW m⁻³ can be captured when 1.0 m³ river water is mixed with 1.0 m³ seawater or with a large surplus of seawater and the global reservation of the osmotic energy is around 2.5 terawatts [2, 3]. However, 980 GW of this osmotic energy is accessible using PRO technique [2]. So far, the development of osmotic power is still in infancy. Compared to other renewable energy techniques (e.g. Wind turbine and Solar cell), PRO has several advantages including stable power out-put and low cost (construction and daily operation).

Using PRO technique to capture the salinity gradient energy was proposed by Sidney Loeb in 1975 [4]. After that, the studies of PRO process for power generation has been continuously conducted from the salinity-energy sources such as the Dead Sea and Great Salt Lake by Loeb and co-workers [5-11].

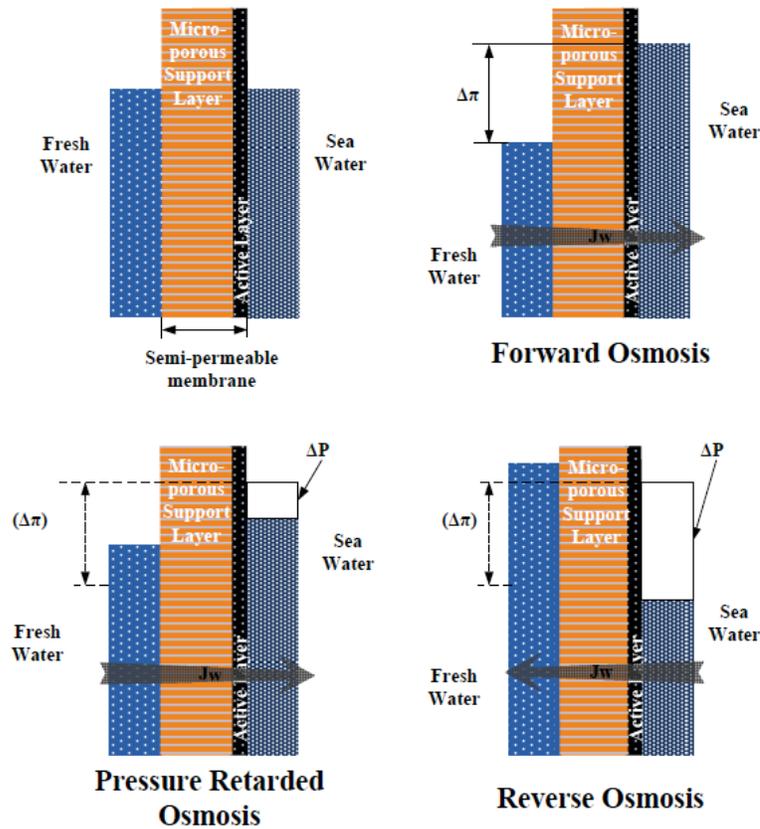
McGinnis *et al.* proposed a closed cycle PRO process (i.e. osmotic heat engine) to exploit the osmotic power generated using a concentrated ammonia-carbon dioxide draw solution [12]. In November 2009, the world first PRO power plant was built with a capacity of 4.0 kW in Tofte, Norway and operated by a leading energy company - Statkraft [13]. They also claimed a full-scale 25 MW osmotic power plant is planned to build by 2015.

THE PRINCIPLE OF PRO

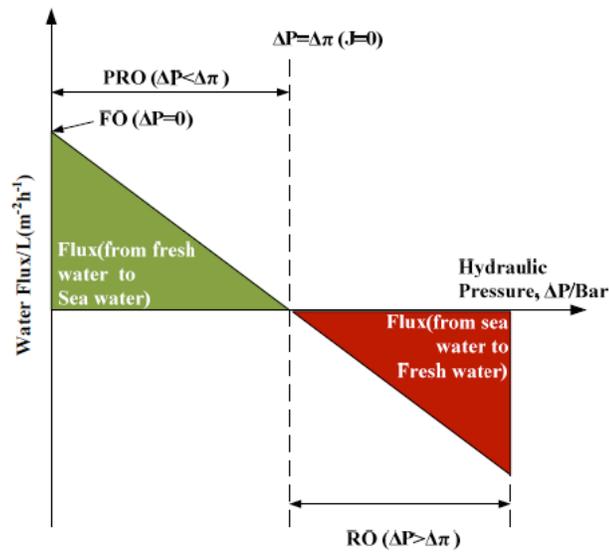
PRO relies on the utilization of large osmotic pressure differentials across semi-permeable membranes to generate water flux. In Figure 1a, the water flux is indicated under different operations including forward osmosis, pressure retarded osmosis and reverse osmosis, respectively. For a FO process, ΔP is zero; for RO, $\Delta P > \Delta \pi$; and for PRO, $\Delta \pi > \Delta P$. Flux directions and driving forces for the three processes were characterized in the early 1980s by Lee *et al.* [14]. The FO point, PRO zone, and RO zone, along with the flux reversal point, are illustrated in Figure 1b.

The principle of PRO power plant can be illustrated in Figure 2a. When seawater (or brine from reverse osmosis) and fresh water (such as river water or secondary fresh water-e.g. waste water) are separated by a semi-permeable membrane, water will diffuse from the feed solution side into the draw solution side which is the seawater side that is pressurized. The pressurized and diluted seawater is then split into two

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(a)



(b)

Figure 1: Schematic diagrams of a) different membrane separation processes, b) plot of water flux with changing pressure across the membrane.

streams: one going through a hydroturbine to generate power by depressurizing the diluted seawater, and the other one passing through a pressure exchanger to assist in pressuring the seawater and thus maintaining the circulation [3]. In a PRO process, power density

(W) is normalized by the membrane area (e.g. m²) and it is commonly used to represent the energy conversion efficiency of the membrane. It can be written as follow:

$$W = J_w \Delta P \tag{1}$$

where ΔP is the hydraulic pressure different across the membrane, J_w is the water flux and it can be expressed by Eq. (2):

$$J_w = A(\Delta\pi - \Delta P) \tag{2}$$

where A is the water permeability coefficient of the membrane and $\Delta\pi$ is the solution osmotic pressure differential across the membrane. Combining Eq. (1) and (2),

$$W = A(\Delta\pi - \Delta P)\Delta P = -A\left(\Delta P - \frac{\Delta\pi}{2}\right)^2 + A\frac{\Delta\pi^2}{4} \tag{3}$$

It can be seen from Figure 2b that when the hydraulic pressure is equal to the half of the osmotic

pressure across the membrane, the power density reaches maximum theoretical value and suggesting the optimal working condition for a PRO power plant. From Eq. (3), the maximum power density value can be obtained as in Eq. (4):

$$W_{max} = A\frac{\Delta\pi^2}{4} \tag{4}$$

MEMBRANE STRUCTURE AND PARAMETERS

The PRO system performance mainly relies on the membrane performance which is determined by the membrane structure. For a skin active layer, A in Eq. (2) represents the ability of water diffuse through the active layer and there is another parameter for

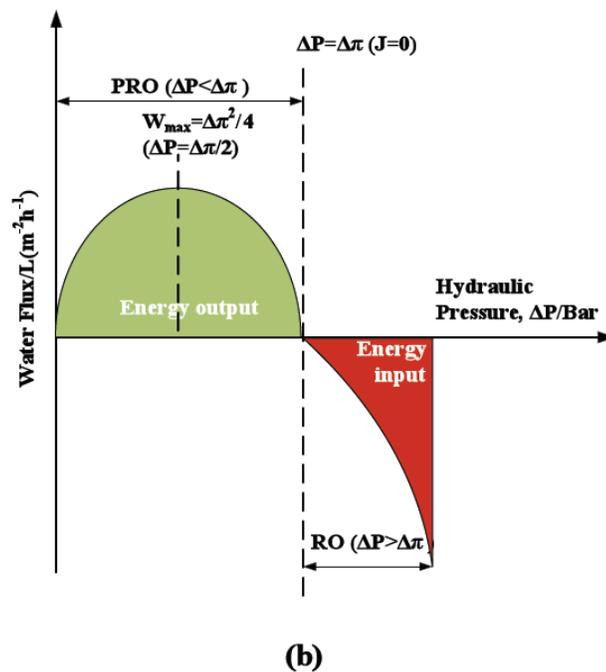
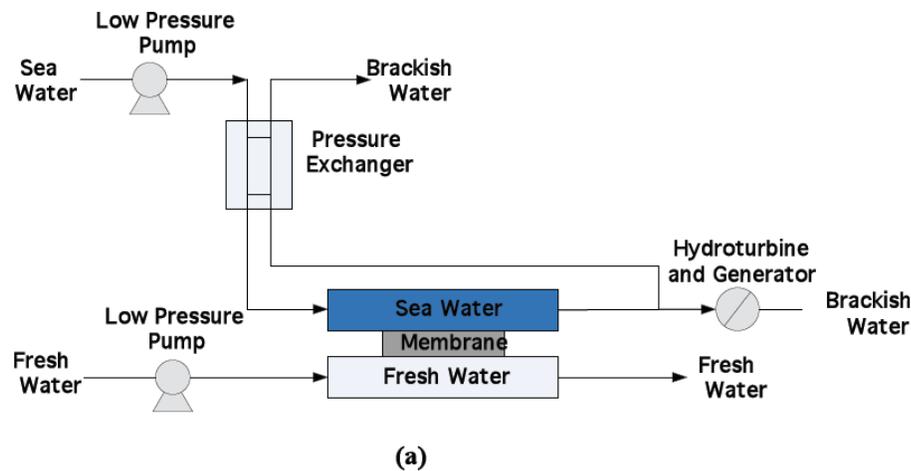


Figure 2: Schematic diagrams of a) PRO power plant and b) Energy consumption/production in FO, PRO and RO using semi-permeable thin film.

evaluation, which is B -the salt permeability, can be described as follow:

$$J_s = B\Delta C_{salt} \quad (5)$$

where ΔC_{salt} is the concentration different of salt between feed and draw solution. In theory, the desired skin active layer should possess a high A and low B , namely high water permeability coefficient and low salt permeability. However, there are many studies suggested that there is strong trade-off between two parameters.

In a thin-film composite membrane, the structure of porous support layer can be expressed using Eq. (6):

$$S = x \times \tau / \varphi \quad (6)$$

where τ is the tortuosity, φ is the thickness of porous support layer, φ is the porosity. In general, the lower the structure parameter S , the better the performance of the membrane under PRO operations is.

CONCENTRATION POLARIZATIONS IN PRO

In osmotic and pressure-driven processes, concentration polarization is a natural phenomenon and it is inevitable. A typical membrane for PRO (in Figure 3) comprises a layer of rejection active layer which is thin (e.g. $<1\mu\text{m}$) and dense, and a micro-porous support layer for providing the adequate mechanical strength. In PRO, the fresh water (feed solution) is directed against the support layer as shown in Figure 3 when osmotic pressure gradients are used to generate electricity [15]. Water transports from the fresh water side to the sea water side. Ideally, the osmotic pressure across the membrane is driven by the concentration difference between the bulk concentration of fresh water $-C_1$ and the bulk concentration of sea water $-C_5$. However, when the fresh water flows on the active layer of the membrane, solutes build up at the active layer that causing the fresh water concentration at the surface of micro-porous layer increase from C_1 to C_2 . This is called concentrative external CP and is similar to the CP in pressure-driven membrane processes (e.g. reverse osmosis) [16]. This CP on the feed side of a membrane is a significant problem in pressure-driven membrane desalination processes. This phenomenon inhibits permeate flow due to an increased osmotic pressure at the membrane active layer interface on the feed side of the micro-porous layer. In an osmotic process, this phenomenon occurs on both sides of the membrane with the effect being dilutive on the permeate side,

namely dilutive CP (decrease from C_5 to C_4). Both concentrative and dilutive external CP can be reduced by deliberately creating turbulence at both sides of the membrane while operating the system unit. It has been suggested that the external CP has a minor effect on the membrane performance [17].

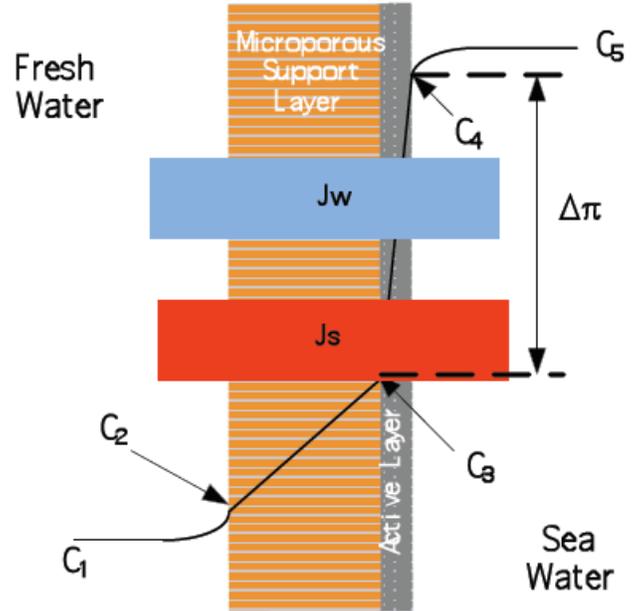


Figure 3: Schematic diagram of the external and internal concentration polarization of the membrane in PRO.

ICP occurs within the micro-porous support layer and leads to the concentration of fresh water at the surface of active layer (feed solution side) increase from C_2 to C_3 . It cannot be mitigated by hydrodynamics such as turbulence and hence drastically reduces the osmotic driving force. So far, it has been established that the water flux decline in FO is predominantly caused by ICP [15, 18-20]. The earliest FO studies found that ICP could reduce the water flux by more than 80 % [21, 22].

The water flux in terms of membrane parameters in PRO processes can be written as following equation [23, 24]:

$$\ln \left[\frac{(A\pi_D - A\Delta P - J_v) + B(A\Delta P / J_v) + 1}{A\pi_F + B((A\Delta P / J_v) + 1)} \right] = \frac{J_v}{K_m} \quad (7)$$

where B is the solute permeability of the semi-permeable active layer; π_D and π_F are the osmotic pressures of the draw solution and the feed water, respectively; K_m is the mass transfer coefficient in the membrane substrate, which is the ratio of solute diffusivity in water (D) over the structure parameter (S) of the membrane support layer. The S is defined as the

product of membrane support layer thickness (l) and tortuosity (τ) over its porosity (ϵ):

$$K_m = \frac{D}{S} = \frac{\epsilon D}{\tau l} \quad (8)$$

Therefore, the power density ($W\ m^{-2}$) can be expressed as:

$$W = J_v \times \Delta P = K_m \ln \left[\frac{(A\pi_D - A\Delta P - J_v) + B((A\Delta P / J_v) + 1)}{A\pi_F + B((A\Delta P / J_v) + 1)} \right] \times \Delta P \quad (9)$$

If there is no hydraulic pressure difference across the membrane, i.e., $\Delta P = 0$, a simplified Eq. (3) can be used to express water flux in the FO process. The above Eq. (9) indicates that the power output from a PRO power plant is mainly depend on the membrane performance when the feed and draw solutions have relatively constant concentration.

In addition, reverse solute diffusion (J_s) (in Figure 3) in osmotically driven membrane processes is also inevitable due to the concentration differences. It has been well established the adverse effects (e.g. membrane fouling) for FO and PRO processes. The details of this phenomenon can be found in previous publications [3, 16, 25, 26].

CELLULOSE ACETATE MEMBRANES

The membrane in the PRO process is the key component. The requirement for a good PRO membrane is high water flux together with a low salt permeability [27]. To make PRO profitable, the power density of the PRO system was determined to be between 4-6 W/m^2 [27]. However, the development of PRO has been hindered for many years by the lack of high performance membrane particularly with adequate water flux. For example, a power density between 0.11 and 1.22 Wm^{-2} was yielded using existing reverse osmosis membranes in a pressure retarded osmosis application on seawater and fresh water (osmotic pressure difference $\Delta\pi = 20$ -25 bar) [28]. The thick support layers of those RO membranes contributed to severe ICP which reduce the water flux and power density [28].

Cellulose acetate has many advantageous characteristics such as relatively high hydrophilicity that favors high water flux and low fouling propensity, good mechanical strength, wide availability and good resistance to degradation by chlorine and other oxidants [3, 29, 30]. The history of using CA as material for membrane separation can go back as early as

1950s [31, 32]. The later breakthrough was made by Loeb and Sourirajan, and the asymmetric CA membrane became viable for membrane separation especially for RO process [33]. Hydration Technology Innovations (HTI) is a leading company on forward osmosis technique. Currently, two types of membrane which are cellulose triacetate (CTA) membrane and thin composite membrane are commercially available from this company. There have been extensive investigations on both membranes. The cross-section image of CTA membrane from HTI is shown in Figure 4. It is thin film (around 50 μm) that consists of a polyester mesh support and CTA active layer. The water flux of CTA membrane from HTI is 18.6 $L\ m^{-2}\ h^{-1}$ using DI water and 0.5 M NaCl as feed solution and draw solution, respectively [34]. The power density of such membrane reached up to 1.3 Wm^{-2} [27].

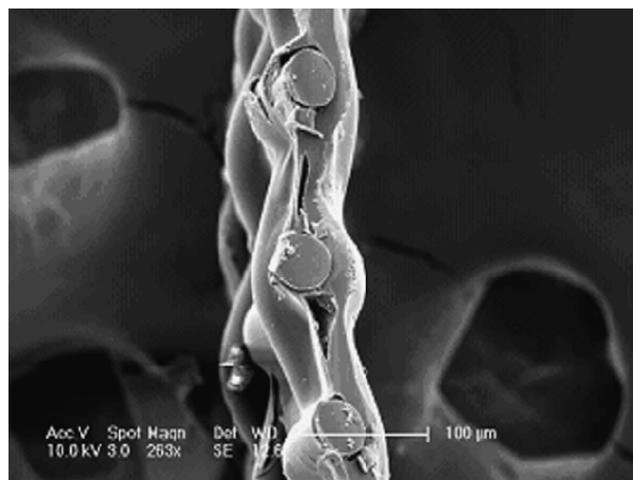


Figure 4: SEM image of the cross-section of CTA membrane from HTI [35].

Lately, Chung and co-workers have developed a number of cellulose ester-based membranes (hollow fiber and flat sheet modules) for FO applications [29, 36-38]. The methods are quite similar for preparing these cellulose derived membranes: phase inversion and then hot water annealing (at 60-95 $^{\circ}C$). They found that the obtained FO membranes have two active skin layers, which are able to reduce ICP effect on the membrane performance and a mathematic model was developed based on this kind of double-skinned FO membrane [29, 37, 39]. The preliminary test showed high water flux which is 48.2 $L\ m^{-2}\ h^{-1}$ and low reverse salt diffusion using quite high concentration of divalent salt solution (5.0 M $MgCl_2$) as draw solution at 22 $^{\circ}C$. The same research group also observed that the interaction between the polymer and the casting substrate, which played an important role in the morphology of the membrane during the preparation

[29]. In addition, Sairam *et al.* used the same phase inversion method to develop flat sheet FO membranes with cellulose acetate [40]. They tried using lactic acid, maleic acid and zinc chloride as pore-forming agents and cast the membrane onto nylon fabric at different annealing temperatures. They found that the prepared membrane using zinc chloride as the pore-forming agent had relatively good FO performance.

The limitations of CA membranes must be taken into account for the development of PRO membrane including the biological attack and solution pH (4-6), temperature ($< 35^{\circ}\text{C}$) due to the hydrolysis propensity.

THIN FILM COMPOSITE MEMBRANES

Recently, various types of flat-sheet of composite and hollow fiber membranes were prepared for FO and PRO applications [34, 41-47]. In general, the strategy of preparing those membranes is based on the techniques for the fabrication of RO membrane, namely the porous support layer and the polyamide thin active layer are prepared using phase inversion method and interfacial polymerization, respectively.

The Elimelech's group in Yale University investigated the morphology effect of polysulfone porous support layer on the membrane performance for FO. Their results suggested that both polymer concentration and the composition of polymer solvent affect the morphology of micro-porous support layer [43]. It appeared that the finger-like macrovoids structure in the support layer is favourable for the FO application. Later, the same composite flat sheet membrane consist of a thin polyamide active layer and polysulfone porous support layer was used for PRO and achieved $5.7\text{-}10.0\text{ Wm}^{-2}$ [2, 47, 48]. The high power density was attributed to the tailored structure of polyamide active layer for the PRO application with moderate reverse solute diffusion and the highly porous structure of support layer [47].

Wang and co-workers prepared a polyethersulfone (PES) hollow fiber substrate and it was incorporated with polyamide active layer to form a PRO membrane as shown in Figure 5 [23]. The water flux of this hollow fiber membrane reached $40.6\text{ L m}^{-2}\text{h}^{-1}$ using 10.0 mM and 5.0 M NaCl solution as feed and draw solution,

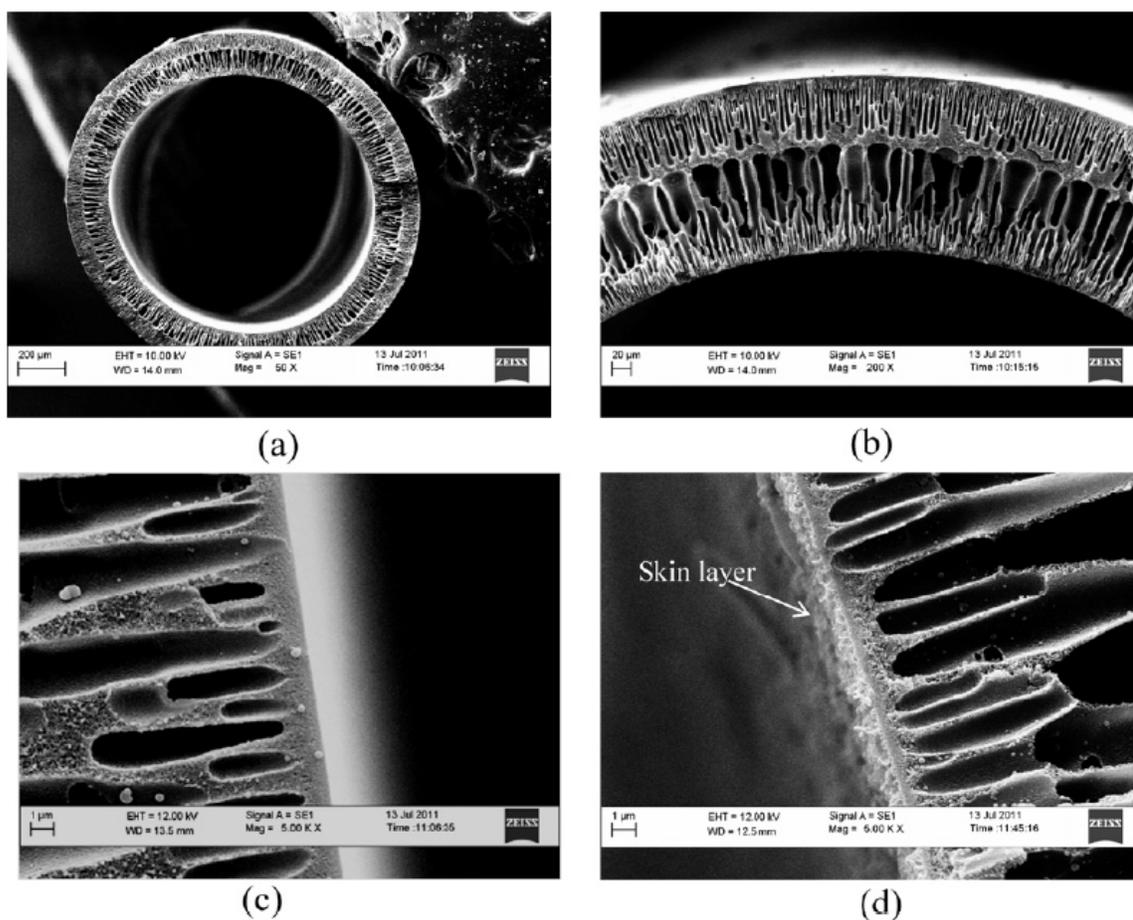


Figure 5: SEM images of hollow fiber membrane [23].

respectively. The simulated power density can be as high as 10.6 W m^{-2} using seawater brine (1.0 M NaCl) and wastewater brine (40.0 mM NaCl). They also investigated the surface of the substrate which suggested that a substrate with <300 kDa Molecular weight cut off (MWCO) should be preferred to obtain a good semipermeable skin [49].

CHALLENGES AND PERSPECTIVES

The development of membrane holds the key to the future of PRO power generation and its success will, in turn, have a great influence on FO for other applications such as desalination, food industry and waste water treatment. So far, the most of significant reports on the membrane development are from Elimelech's group in Yale University and research groups from Singapore. TFC membranes are promising for the PRO application in terms of water flux and power density. The state of the art TFC membranes yield over 10.0 W m^{-2} which much higher than the expected value (5 W m^{-2}), and this stimulates a great motivation for building power plant based on these membranes. However, Logan and Elimelech pointed out that the energy consumption needs to be taken into account for pre-treating the fresh water and sea water in order to avoid membrane fouling. Thus, it is critical to improve the contamination resistance of the membrane, particularly the active skin layer [2]. There hasn't been any open literature reports such issue in details and how is it going to affect a PRO power plant in technical and economical ways.

Based on above discussions, the following suggestions are given in order to develop high performance PRO membranes:

- Reduce the ICP from micro-porous support layer

There are still not enough reports on the support layer to cover all the aspects that may affect the water flux, e.g. only few reports on the hydrophilicity of the porous support layer. The higher water flux is beneficial to reduce the membrane fouling in membrane separation processes.

- Novel skin active layer

Most of reports are using PA as active layer and such material has been approved to be sensitive to chlorine and other oxidants from previous RO studies. To implement this membrane for PRO applications, it is critical to develop new skin active layer with high

resistance of contaminations as well as biological fouling.

- ECP, module configuration

ECP starts becoming predominant for future PRO applications due to higher water flux of the membrane. In RO, there are numerous studies on operational procedures. However, the water flux in RO processes is much lower than PRO using the state of the art TFC membranes. It is important to investigate the new module design as well as operating procedures.

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