Ways to increase porosity in the support layer are (1) reducing the polymer concentration, (2) adding pore-forming agents such as ethylene glycol (EG), calcium chloride and polyvinylpyrrolidone (PVP) into dopes, and (3) using weak non-solvents as the coagulant media (Yang et al. 2009; Li et al. 2012).

Hydrophilicity plays an important role in affecting ICP. When the substrate is hydrophobic, it is difficult to be wetted by aqueous solutions. The pores that are not wetted by water are not available for the transport of water and solute molecules. Therefore, the effective area for mass transport is reduced. More severe ICP is resulted and a lower water flux is observed. Studies have demonstrated that by increasing the hydrophilicity of the support layer, the performance of FO membranes could be largely enhanced (Widjojo et al. 2011; Arena et al. 2011; Han et al. 2012a, Wang et al. 2012; Widjojo et al. 2013).

#### 8.2.3 Membrane Characterization

Usually, FO membranes are characterized by their water flux, solute reverse flux as well as structural parameter. Fundamental transport properties such as water permeability and salt permeability of the membrane materials are important to fully understand the transport properties and mechanisms.

The water permeability and salt permeability can be determined in a pressuredriven process (Zhang et al. 2010). At a given hydraulic pressure  $\Delta P$  (usually lower than 10 bar to ensure that the membrane structure is similar to the one in the FO process), deionized (DI) water is used as the feed and the permeate is collected to get the water permeability using the following equation:

$$A = \frac{\Delta V}{S_m \Delta t \Delta p} \tag{8.22}$$

where  $\Delta V$  is the volume of permeated water across the membrane area  $S_m$  in a certain time period  $\Delta t$ . Meanwhile, the salt rejection is tested using a low concentration salt solution (usually 100–5, 000 ppm) as the feed:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{8.23}$$

The salt concentrations  $C_f$  and  $C_p$  in the feed and permeate, respectively, can be determined using a conductivity meter. Then the salt permeability *B* could be calculated based on eq. (8.24) where  $\Delta \pi$  is the osmotic pressure difference between the feed and permeate in the pressure-driven process:

$$B = \frac{1-R}{R} (\Delta P - \Delta \pi) A \tag{8.24}$$

In a lab-scale FO setup, membrane modules/cells are fixed in the middle of the setup, with feed and draw solutions flowing counter-currently at either side the membranes in the cross-flow mode. To standardize the membrane performance so

#### This is a preview. Click here to purchase the full publication.

that different experiments can be compared, 1M or 2M NaCl solution is commonly used as the draw solution, and DI water is the feed. The water permeation flux ( $J_w$ , L·m<sup>-2</sup>·hr<sup>-1</sup>, abbreviated as LMH) is calculated as below:

$$J_w = \frac{\Delta V}{S_m \Delta t} \tag{8.25}$$

The conductivity of the feed solution is recorded and salt reverse flux from the draw solution to the feed,  $J_s$  in g·m<sup>-2</sup>·hr<sup>-1</sup> (abbreviated as gMH), is determined from the increase in conductivity of the feed:

$$J_s = \frac{\Delta C_t V_t}{A\Delta t} \tag{8.26}$$

where  $\Delta C_t$  is the concentration change of the feed during the testing period, and  $V_t$  is the volume of the feed at the end of the test. Data in both PRO and FO modes can be tested by simply changing the membrane orientation. Once water and salt permeability, and water flux in the FO mode are known, structural parameter can be calculated from eq. (8.27):

$$S = \frac{D}{J_{w}} \ln \frac{A\pi_{D,b} + B}{A\pi_{F,m} + J_{w} + B}$$
(8.27)

# 8.3 INTEGRALLY SKINNED ASYMMETRIC MEMBRANES BY PHASE INVERSION

Integrally skinned asymmetric membranes are formed by phase inversion where the dense skin layer and porous sublayer are made of the same material and formed in a one-step process. Figure 8.3(A) schematically depicts the cross-sectional views of two typical integrally skinned membranes.

The formation of integrally skinned asymmetric membranes via nonsolvent induced phase inversion was first demonstrated by Loeb and Sourirajan using CA



Figure 8.3. Schematic illustration of integrally skinned asymmetric (A) flat sheet membrane and (B) hollow fiber membrane structures

This is a preview. Click here to purchase the full publication.

as the material (Loeb and Sourirajan 1964). They prepared a CA polymer solution containing acetone as the solvent and water and magnesium perchlorate as additives and cast evenly on a glass plate with a controlled thickness using a doctor blade. After subjecting to evaporation in air for a short duration, the as-cast membrane was then immersed in a water bath for nonsolvent induced phase inversion. The resultant membrane has the structure depicted in Figure 8.3(A). This type of membranes has been widely used in reverse osmosis (RO) applications. The study of integrally skinned FO membranes only took place about 10 years ago (Wang et al. 2007; Herron 2008].

By optimizing the chemistry of coagulants and casting plates as well as dope formulation, flat sheet membranes with various structures can be designed (Wang et al. 2010; Zhang et al. 2011; Ong et al. 2012). Similarly, integrally skinned hollow fiber membranes can be tailored made using the same concept (Wang et al. 2007; Su et al. 2010a & b) by choosing an appropriate external coagulant and a bore fluid as well as spinning conditions. Basically, a strong non-solvent coagulant such as water tends to induce a dense selective skin, while a weak non-solvent or solvent/ non-solvent mixture tends to induce a sponge-like morphology as the support layer structure. A typical single layer hollow fiber membrane with a dense selective skin at the outer layer is depicted in Figure 8.3(B).

### 8.3.1 Cellulose Ester Membranes

Among all available polymers in the market, cellulose ester polymers, especially CA, have received the most attention as FO membrane materials due to vast availability, low costs, hydrophilicity, ease of fabrication and also chlorine resistance. Cellulose esters are green polymers as they are easily derived from esterification of cellulose with acetic acid, a commonly found natural organic compound. The Hydration Technology Innovations, HTI was the first to develop and manufacture CTA-based FO membranes with woven supports in the market (Herron 2008). The woven support is relatively porous and the membrane has an asymmetric structure formed via phase inversion as shown in Figure 8.4(A). This membrane achieves a superior FO performance than those standard RO membranes due to relatively thinner membrane thickness and more porous support structure.

Following the success of HTI CTA FO membranes, several CA FO membranes have been developed. The most widely explored cellulose ester is CA which has an acetyl content of less than 40 wt% and has high hydrophilicity. Its inherent free volumes in dry and wet states and water transport properties have been studied for in depth for both RO and FO (Zhang et al. 2012).

Among many CA FO membranes, the double-skinned CA membrane without support fabrics, as shown in Figure 8.4(B), has gained much attention due to its unique design which mitigates ICP and fouling phenomena. Contrary to the conventional Loeb-Sourirajan phase inversion membranes, the double-skinned CA membranes were invented by a slightly different method. Most conventional phase inversion membranes designed have dense selective skins on top of the asymmetric membranes via fast evaporation and outflow of solvent.



Figure 8.4. Cross-section images of (A) HTI CTA and (B) double-skinned CA membranes

However, the double-skinned CA membranes were fabricated without the solvent evaporation step (Wang K.Y. et al. 2010; Zhang et al. 2010; Ong et al. 2012). After casting the polymer solution on the glass plate, it was immersed into a water coagulation bath at room temperature immediately. The resultant double-skinned membranes has a distinctive three-layer structure consisting of a top loose dense skin with a larger mean effective pore size, a thick fully open cell porous middle layer and a thin dense bottom skin which has a small mean effective pore size to reject small solutes such as NaCl ions.

The top skin was formed due to (1) the rapid solvent evaporation during the casting as acetone was used as the solvent following by (2) the rapid solvent outflow to the coagulant when the nascent membrane was immersed into the coagulation bath. Thus the polymer concentration at the top skin increased rapidly and formed a relatively dense top skin. The fully porous middle layer was resulted from the delayed demixing in the bulk after the formation of the top dense skin. The bottom dense selective skin was formed via a hydrophilic-hydrophilic interaction between CA which has a high content of hydroxyl group and the hydrophilic glass casting substrate. During phase inversion, CA molecules near the bottom surface were in contact with the glass plate and due to the hydrophilicity of both CA and glass plate, the CA molecules would adhere on the glass surface and aggregate to form the bottom selective skin. With heat treatment in DI water as the post treatment, the double-skinned CA membranes achieved a high rejection towards NaCl ions.

CA FO membranes with a double-skinned structure have been tested and compared against single-skinned CA FO membranes (Zhang et al. 2010) using a colloidal feed solution containing aluminum oxide nanoparticles. The former has a significantly lower flux reduction due to less fouling than the latter. In addition, the backwashed membranes of the former have a higher recovered water flux than the latter. Clearly, the top loose dense layer of the double-skinned membranes can effectively prevent irreversible fouling where particles may trap easily within the membrane porous layer which is difficult to be removed by simple flushing. The advantages of the double-skinned structure for FO applications have been mathematically confirmed by Tang and his coworkers where they modeled the transport mechanism for double-skinned FO membranes by modifying the existing solution-diffusion model for single-skinned FO membranes (Tang et al. 2011).

Besides, integrally double-skinned hollow fiber membranes have been developed using CA (Su et al. 2012) to produce FO hollow fiber membranes with less susceptible to ICP and fouling. The dense inner selective skin was formed by using pure water as the bore fluid to induce instantaneous demixing. The outer skin was made with slightly looser pores by using a 50/50 wt % NMP/water coagulant to induce a slower incomplete demixing at first before the nascent fiber entered the external water bath. The inner selective skin was further heat treated by circulating 90°C DI water at the lumen side of the hollow fiber to improve the skin's selectivity as well as FO flux.

The post heat treatment is important to tailor CA FO membranes with proper pore sizes no matter the membranes are single- or double-layer and flat sheet or hollow fiber configurations. A two-step heat treatment, i.e., 60 min at 60°C and 20 min at 95°C using a DI water bath, was found effectively to shrink the membrane effective mean pore size of CA nanofiltration hollow fiber membranes for FO processes (Su et al. 2010a). Fundamental studies have revealed that heat treatment effectively increases FO water flux due to (1) the shrinkage of pore sizes and (2) the reduction of reverse salt flux to the feed solution which would otherwise lead to a drastic drop in the effective driving force (Su et al. 2010b). However, heat treatment at very high temperatures leads to a drop in water flux due to pore tightening that causes a high resistance for water transport.

Since CA has poor resistance towards biodegradation and a narrow pH operation window due to poor hydrolytic stability, other cellulose esters such as CTA, cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) have also been explored as materials for FO membranes (Ong et al., unpublished manuscript 2013). CTA are cellulose esters containing very little or no content of hydroxyl functional groups while CAP and CAB have both hydroxyl and propionyl groups and hydroxyl and butyryl groups, respectively. Because of very little hydroxyl content, CTA is excellent in terms of hydrolytic stability and biodegradation resistance. FO membranes fabricated using CTA and CTA/CA blends have shown much higher salt resistance than pure CA FO membranes but at a tradeoff of lowering water flux. This is due to the higher CTA chain entanglement which results in the dense selective skin with a dense and highly packed structure (Ong and Chung 2012). Higher CTA content in CTA/CA blend FO membranes also lead to a higher rejection towards NaCl ions (Nguyen et al. 2013). Therefore, CTA is an excellent FO membrane material when a high selectivity is required. However, it is difficult to process CTA because of limited solvents available to dissolve it. CAP and CAB offer much more control over the desired FO membrane performance as the content of functional groups can be varied as depicted in Figure 8.5.

By tuning the content of various functional groups in the cellulose ester, the FO performance of the resultant membranes can significantly change (Ong et al. 2012 & unpublished manuscript 2013; Stamatialis et al. 2000). FO membranes



Figure 8.5 Repeating unit and various functional groups of cellulose esters

made from cellulose esters with very high hydroxyl content tend to have high water and solute permeability due to their relatively more hydrophilic. Since solutes alone cannot transport through the membranes without the aids from a solvent, the high water permeability across the membrane also facilitates a high solute transport. The bulkier and longer functional groups such as propionyl and butyryl groups are relatively more hydrophobic than hydroxyl and acetyl groups. Therefore, an increase in propionyl and butyryl content would result in cellulose ester membranes with higher hydrophobic and selectivity. On the other hand, high content of bulky propionyl and butyryl also causes an expansion in free volume and voids and reduces selectivity. To counter-balance these opposite effects, a moderate content of hydroxyl and propionyl or butyryl groups is preferred to achieve a reasonable FO water flux and solute rejection.

Though the CAP and CAB FO membranes exhibit better FO performance in terms of solute rejection, they still have the disadvantage of being relatively more hydrophobic. Therefore, dual layer hollow fiber membranes made of thin CAP or CAB selective skin layer on a thick and porous CA layer have been proposed (Su et al. 2013). Using CA as the material for the porous support layer offers a few advantages including high porosity and high hydrophicility which improve better water permeation whereas a selective skin layer made of CAP or CAB enhances the selectivity of the membrane.

# 8.3.2 Polybenzimidazole Membranes

Apart from cellulose esters, polybenzimidazole (PBI) is also a popular choice of materials for FO membranes. PBI offers some advantages over cellulose esters including excellent chemical resistance, high temperature stability and charged characteristics in aqueous environments. The chemical structure of PBI is shown in Figure 8.6.

PBI nanofiltration hollow fiber membranes were used for FO in the earlier research. However, this type of membranes did not have a good rejection towards monovalent ions such as NaCl even though the rejection towards divalent ions was high (Wang et al. 2007). Therefore, cross-linking of PBI selective skin using *p*-xylene dichloride was carried out to tailor the pore size and enhance the selectivity



Figure 8.6. Chemical structure of polybenzimidazole (PBI) and cross-section morphology of the dual layer PBI hollow fiber membrane for FO

(Wang et al. 2009). Since pure PBI membranes are brittle and difficult to handle, dual layer hollow fiber membranes were then invented via coextrusion technique to solve this problem. A thin selective layer made of PBI was fabricated on a thick and porous polyethersulfone (PES) support in a one-step process (Yang et al. 2009). This not only eliminated the handling problem of PBI membranes, but also significantly reduced the material cost. Besides, the dual-layer structure can effectively mitigate ICP effects if one can design its sublayer with a fully porous structure. A cross sectional image of a dual layer hollow fiber membrane is shown in Figure 8.6.

Flat sheet FO membranes made from PBI were also evaluated. Surface modifications were conducted to increase hydrophilicity and surface charge of PBI membranes. The use of 4-(chloromethyl) benzoic acid (CMBA) as activator and *p*-phenylene diamine, ethylene diamine and taurine for the functionalization of the membrane surface resulted in increase in hydrophilicity and membrane surface charge (Flanagan et al. 2011; Hausman et al. 2010). Recently, poly (acrylamide-co-acrylic acid) (PACA) was also used to functionalize PBI flat sheet membranes (Flanagan and Escobar 2013). From the zeta-potential tests, the functionalized PBI membranes had more charged surfaces than the virgin PBI membranes. The contact angles of the PBI membranes were also reduced significantly after functionalization indicating an increase in hydrophilicity which is favorable for FO applications.

# 8.3.3 Polyamide-imide Membranes

In recent years, Setiawan et al. (2011) employed polyamide-imide (PAI) as the base material to fabricate hollow fiber membranes for FO. The nascent PAI membrane has an ultrafiltration (UF) – like skin layer. Since PAI polymers can be easily crosslinked by polyethyleneimide (PEI) molecules, the membrane was modified to reduce its pore size of the selective layer. The degree of crosslinking was highly dependent on the molecular weight of PEI, PEI concentration, crosslinking time and temperature. The resultant membrane showed a poor rejection to NaCl, but reasonably good rejections to divalent ions. To avoid the excessive crosslinking in the supporting layer and to save the costly PAI material, PAI–PES dual layer hollow fiber membranes were developed (Setiawan et al. 2012a). PAI was the outer selective layer, while PES was the inner support layer. Similar to the case of PBI-PES dual hollow fiber membranes (Yang et al. 2009), the dual-layer PAI-PES membrane exhibited a better water flux than the single-layer one. However, this type of membranes is not efficient for NaCl rejection and hence can be mainly applied to the applications where no NaCl is involved.

Since the PEI-modified PAI hollow fiber membrane is positively charged which might induce severe fouling during applications. Therefore, a negatively charged polystyrene sulfonate sodium salt (PSS) was deposited on top of the PEI layer to alter its surface electrochemical properties (Setiawan et al. 2012a). Flat sheet membranes with a positively charged selective layer were also fabricated suing the same material on a woven fabric (Qiu et al. 2012).

# **8.4. COMPOSITE MEMBRANES**

Composite membranes are usually prepared in two consecutive steps: the fabrication or selection of a proper supporting substrate and the coating of a thin selective layer onto the support by spin coating, on-site reaction, dip coating, etc. The interactions between the two layers might involve covalent bonding, electrostatic interaction or van der Waals force. The major advantage of composite membranes over integrally skinned membranes is the freedom of independent control of both layers to optimize the structure and maximize the performance for each specific application, i.e., the thickness, pore size, porosity and chemistry of each layer could be independently tailored. This is especially useful for FO membrane development since a fully porous support layer and a highly permeable and selective dense layer are required.

So far, three different types of composite membranes have been developed for FO, including thin film composite (TFC), layer-by-layer (LbL) and biomimetic membranes. The TFC membrane is the most important and common type of composite membranes for RO. Depending on the monomers used, the same interfacial polymerization technology could also be applied for NF. In other words, the selectivity of the thin dense selective layer can be designed for different applications. Therefore, this type of membrane holds a great potential for the

desalination, wastewater treatment and many other separation purposes via FO. Another type of composite membranes for water separation is the LbL membrane. The selective layer is formed through the electrostatic interaction between different polyelectrolytes. The traditional LbL membranes are mainly designed for ultrafiltration (UF) and NF processes, and it is also possible to fabricate LbL membranes for some FO processes where large molecules are involved. Usually LbL membranes do not have sufficient rejection towards NaCl. The biomimetic membranes intend to mimic biological cell membranes to achieve high permeability and selectivity. Recent studies have shown their great potential for water reuse and desalination but their mechanical stability needs improvements for practical applications. Table 8.1 provides a list of the FO performance of the representative membranes developed in recent years.

#### 8.4.1 Thin Film Composite Membranes

Thin film composite (TFC) membranes made of interfacial polymerization have gained considerable attention in the recent FO development and studies. Whilst the early concept of TFC membranes through interfacial polymerization (IP) was reported by Mogan in the 1960s (Morgan 1965), the major breakthrough on the fabrication of TFC membranes for various applications was discovered by Cadotte in the 1970s (Cadotte 1977; Cadotte et al. 1980; Cadotte 1981). Since then, TFC membranes have dominated the production of modern reverse osmosis (RO) and nanofiltration (NF) membranes (Petersen 1993; Verissimo 2005; Ghosh et al. 2008). Generally, TFC membranes consist of a top thin polyamide selective layer and a porous membrane support. The formation of a thin layer of polyamides can be attained via in-situ interfacial polymerization between two monomer solutions such as an aqueous polyfunctional amine solution, e.g. *m*-phenylenediamine (MPD) monomer, and a polyfunctional acyl chloride, e.g. trimesoyl chloride (TMC) monomer dissolved in an apolar organic solvent, e.g. hexane.

Because of solubility preference of monomers in two different phases, the aqueous and organic phrases are immiscible. The IP reaction takes place extremely fast (even less than one minute) at the organic phase near the interface, subsequently leading to form a dense polyamide thin film layer on top of the membrane support. Figure 8.7 shows a diagram of an interfacial polymerization between MPD and TMC monomers and the resultant TFC layer with a typical unique ridge and valley morphology.

In comparison with other integrally skinned membranes in terms of RO performance, the TFC membranes tend to exhibit a superior water permeation flux, greater solute rejection and better non-biodegradability (Roh and Khare 2002; Rao et al. 2003; Jin and Su 2009). Despite the fact that TFC membranes developed through IP are applicable for FO membranes, the fabrication schemes and optimizations for FO and RO membranes via IP are quite different. This is due to the fact that they have different essential requirements on their membrane support. RO membranes need a mechanically strong and robust supporting layer to withstand high transmembrane pressures (60–100 bars) during RO operation, whereas FO membranes need a thin and fully porous support layer to reduce ICP.

Table 8.1. A list of FO performance of representative phase inversion and composite membranes. DI water was used as the feed and tests were conducted at 20–25 °C.

Membrane	Water flux Lm <sup>-2</sup> h <sup>-1</sup> (FO/PRO)	Reverse salt Flux, gm <sup>-2</sup> h <sup>-1</sup> (FO/PRO)	Draw solution	Ref
HTI flat sheet CA double-skin flat sheet	13.0 (FO) 22/32	10.5 16/25	2.0 M NaCl 2.0 M NaCl	Phillip et al. 2010 Wang KY et al. 2010
CAP-CA dual layer hollow fiber	8.5/17.5	1/2	2.0 M NaCl	Su et al. 2013
PBI-PES dual layer hollow fiber	24.5/33.8	0.45/0.5	5.0 M MgCl <sub>2</sub>	Yang et al. 2009
PAI-PES dual layer hollow fiber	15.5/27.5	5.5/83.7	0.5 M MgCl <sub>2</sub>	Setiawan et al. 2012
TFC PES hollow fiber	29.5/68.0	2.6/5.8	2.0 M NaCI	Chou et al. 2010
TFC-PES hollow fiber	34.5/65.1	9.87/12.34	2.0 M NaCl	Sukitpaneenit et al. 2012
TFC-PESU E6020P flat sheet	62.8/78.8	14.9/13.5	2.0 M NaCl	Widjojo et al. 2013
LbL flat sheet	48/98	16/47	2.0 M MgCl <sub>2</sub>	Qiu et al. 2011
LbL flat sheet	11.6/11.8	8.1/13.0	0.5 M NaCl	Duong et al. 2013
Biomimetic flat sheet	142 (PRO)	6.2	2.0 M NaCl	Wang H et al. 2012