

PDF issue: 2025-06-13

Development of polyamide thin-film composite polyvinylidene difluoride hollow fiber forward osmosis membrane and its commercialization strategy

Yabuno, Youhei

<mark>(Degree)</mark> 博士(科学技術イノベーション)

(Date of Degree) 2021-03-25

(Date of Publication) 2022-03-01

(Resource Type) doctoral thesis

(Report Number) 甲第8097号

(URL) https://hdl.handle.net/20.500.14094/D1008097

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**Doctoral Dissertation** 

# Development of polyamide thin-film composite polyvinylidene difluoride hollow fiber forward osmosis membrane and its commercialization strategy

ポリアミド薄膜複合ポリフッ化ビニリデン中空糸型正浸透膜の開発 とその事業化戦略

January 2021

Graduate School of Science, Technology and Innovation Kobe University

Youhei Yabuno

# Contents

С	hapter I General Introduction	1
	I.1. Back ground	1
	I.2. Membrane in water treatment	3
	I.2.1. History of water treatment membrane technology	3
	I.2.2. Classification of water treatment membrane	5
	I.2.3. Technology changes in reverse osmosis (RO) technology	7
	I.3. Forward osmosis (FO) technology	10
	I.3.1. Advantages of FO technology compared with RO technology	10
	I.4. Remaining problems of FO membrane	15
	I.4.1. Technology changes in FO membrane	15
	I.4.2. Thin Film composite FO membrane	17
	I.4.3. To produce high performance FO membrane	18
	I.5.Purpose of this study	.20
	I.6.Scope of this thesis	21
	References	.23

# Chapter II Principle of phase separation structure control technology for porous PVDF

sı	ıpport layer	26
	II.1. Introduction	26
	II.2. Experimental	28
	II.2.1. Materials	28
	II.2.2. Measurement methods for LCST and UCST	28
	II.2.3. Measurement methods for crystallization temperature	28
	II.2.4. Preparation method for the surface structure observation sample	29
	II.3. Results and discussion	30
	II.3.1. Effect of PEG as polymeric additive in phase separation process	30
	II.3.2. Effect of PVP as polymeric additive in phase separation process	31
	II.3.3. Surface structure of cast film	34
	II.4. Summary	38
	References	39

Chapter III Preparation of FO membrane with high strength and hydrophilic I	PVDF hollow
fiber membrane support	42
III.1. Introduction	42
III.2. Experimental	44
III.2.1. Materials and chemicals	44
III.2.2. Preparation of PVDF and PSf support layers	44
III.2.3. Interfacial polymerization on porous hollow fiber membranes	46
III.2.4. Membrane characterization	46
III.2.5. RO and FO performance measurement	47
III.3. Results and discussion	51
III.3.1. Characterization of the support hollow fiber membranes	51
III.3.2. Characterization of interfacial polymerized PA hollow fiber membranes	57
III.3.3. RO and FO performance of a TFC membrane	
III.3.4 Comparison of RO and FO performances obtained in this work with those	reported in the
literature	63
III.4. Conclusions	65
References	67
Chapter IV Preparation of high performance FO membrane using a highly pholow fiber membrane support	oorous PVDF
IV.1. Introduction	
IV.2. Experimental	
IV.2.1. Materials	
IV.2.2. Fabrication of PVDF hollow fiber membranes	75
IV.2.3. Preparation of PA-PVDF membranes	77
IV.2.4. Characterization of membranes	77
IV.2.5. FO test conditions for PA-PVDF hollow fiber membranes	
IV.3. Results and discussion	80
IV.3.1. Formation of interconnected bicontinuous structure on PVDF hollow fib	er membranes
	80
IV.3.2. Characterization of PVDF hollow fiber membranes	
IV.3.3. Characterization of PA-PVDF hollow fiber membranes	
IV.3.4. FO performances of PA-PVDF hollow fiber membranes	
IV.4. Conclusions	
References	

Chapter V Commercialization strategy	104
V.1. Remaining problems on commercialization	
V.2. Challenge to zero liquid discharge (ZLD) market	
V.3. Environmental analysis of FO/ZLD system	107
V.3.1 External environmental analysis	107
V.3.1.1 PEST analysis	107
V.3.1.2 5 forces analysis	110
V.3.2 Internal environmental analysis	113
V.3.2.1 Value chain analysis	113
V.3.2.2 VRIO analysis	115
V.3.2.2 Summary of environmental analysis	
V.4. Business model	
References	
Chapter VI Conclusions	
List of publications	127
List of presentations	
Acknowledgement	

# **Chapter I General Introduction**

# I.1. Back ground

The expansion of irrigation facilities due to the global population increase and escalating industrialization and urbanization caused by the economic development of emerging countries has led to a global increase in water demand. Thus, serious water shortages in the future pose a concern. According to the United Nations World Water Development Report (2018), by 2050, the global population will reach 10 billion, but half of this population would suffer from water shortage (Figure I.1) [1]. In 2015, the UN Summit proposed the "sustainable management and use of water and hygiene for all people" as one of the 17 Sustainable Development Goals (SDGs). As such, water-related issues and their solutions are a global responsibility [2].



Figure I.1 Global water scarcity prediction for 2050 [1].

The amount of water consumed per capita increases as the standard of living improves. The 20<sup>th</sup> century witnessed rapid urbanization and industrialization, leading to a rise in global water use well above the rate of population increase (Figure I.2). The main uses of water are agricultural (70%),

industrial (20%), and domestic (10%); however, in the future, the economic development of emerging countries is expected to further boost water demand for industrial and domestic uses [3]. Currently, the severity of water pollution is increasing due to economic development, reducing access to clean and convenient water sources for people. In emerging countries particularly, domestic water use and the generated volume of wastewater are on the rise due to urbanization. Yet, sewage and wastewater treatment facilities are not being developed to keep pace. The expansion of agricultural activities and increased production have resulted in enhanced salt runoff from fertilizers to water bodies such as rivers, leading to eutrophication. In addition, the increase in the generated volumes of industrial wastewater due to rampant industrialization has highlighted the issue of worsening water pollution. Since the inland areas of countries such as China, the US, and India have limited water sources at the outset, the negative impacts of water pollution become even more evident.



Figure I.2 Changes in the global population and water intake [3].

#### I.2. Membrane in water treatment

#### I.2.1. History of water treatment membrane technology

The primary causes of water-related problems are the lack of water and the deterioration of water quality. These problems may be solved by 1) promoting desalination of water with salt content (such as seawater), 2) treating wastewater and then releasing it to the natural environment, 3) recycling wastewater, and 4) reducing the generated volumes of wastewater. To achieve these ends, water processing technology that can remove salt and pollutants efficiently from water is necessary. One new water treatment method in particular, called "water treatment membrane technology," is garnering attention.

The study of water treatment membranes was pioneered by a scientist named Jean-Antoine (Abbé) Nollett. In 1748, he observed that when a pig bladder was sealed and immersed in water, water entered the bladder despite the lack of visible pores in its membrane (i.e., permeation occurred through a semi-permeable membrane) [4]. Since the 1950s, Western scientists have been manufacturing artificial semi-permeable membranes that allow for the permeation phenomenon [5].

Among the various studies being conducted on water treatment membranes at that time, the theory of "semi-permeable membrane or reverse osmosis (RO)," presented by Prof. Charles E. Reid of the University of Florida, captured the interest [6]. The RO membrane functions by artificially creating a phenomenon opposite to that of water transfer by a semi-permeable membrane. Typically, when water with high salt content and pure water are separated by a semi-permeable membrane in a container, pure water migrates to the compartment containing the water with the high salt content, and this migration stops when the concentration of the salt in the water reaches a certain level. This phenomenon is known as "osmosis," and the difference in the water level at this time is called osmotic pressure. However, if pressure higher than the osmotic pressure is applied to the water with the high salt content, the water in the salt solution migrates to the side of the container filled with the pure water. This migration is called "reverse osmosis." Using this principle, pure water could be obtained from seawater by the application of pressure with a pump (Figure I.3).



Figure I.3 The phenomena of osmosis and reverse osmosis.

At the time of the discovery, the US was experiencing a severe water shortage caused by the pumping of groundwater. In 1952, the Office of Saline Water was established within the US Department of the Interior, and seawater desalination technology was studied as a national project. In order to efficiently obtain pure water from seawater at an osmotic pressure of ca. 25 bar, a pressure of at least 50 bar must be applied to seawater. Professor Reid achieved a salt separation performance of 98% with a semi-permeable membrane made of cellulose acetate. However, the water permeation performance (permeability) was low, and it lost its separation performance within several weeks. Thus, this product was never put to practical use. The research group of Sidney Loeb and Srinivasa Sourirajan at the University of California solved this problem, allowing the membrane technology to be put into practice [7]. In 1960, they successfully manufactured a high-performance asymmetrical semi-permeable membrane using cellulose acetate. They achieved high salt separation performance, water permeability, and pressure resistance. As a result, the group at the University of

California began testing water treatment membranes at a pilot plant in 1965.

#### I.2.2. Classification of water treatment membrane

Water treatment membranes are categorized by the membrane pore diameter (separation accuracy). Below, we describe these membranes, using the definitions provided by International Union of Pure and Applied Chemistry (IUPAC) as the reference [8]. We summarize the relationship between types of water treatment membranes, pore diameters, and substances targeted for removal (Figure I.4).

1) Microfiltration (MF) membranes

MF membranes can separate and remove substances sized  $0.1-1 \ \mu m$  from the process liquid. Bacteria comprise the primary separation target. These membranes are used to treat drinking water or produce reused wastewater.

2) Ultrafiltration (UF) membranes

UF membranes separate and remove substances sized 2 nm–0.1 µm from the process liquid. Viruses and proteins are the primary separation targets. In addition to treatment of drinking water and the production of reused wastewater, these membranes are used for medical purposes and concentration/separation processes in the food industry. Separation performance is expressed with a molecular weight cutoff (the size of molecule that can be separated). Membranes with molecular weights ranging from 1,000–300,000 are commercially available.

3) Nanofiltration (NF) membranes

NF membranes separate and remove substances smaller than 2 nm in size from the process liquid. This size range lies between that of the UF and RO membranes. Such membranes were called "loose RO membranes" in Japan. The molecular weight cutoff ranges from 200–1,000. The filter coefficient for NaCl is said to be 90% or less.

4) Reverse osmosis (RO) membranes

RO membranes separate and remove substances sized smaller than 2 nm from the process liquid. They do not allow any dissolved solutes to pass through. The filter coefficient for NaCl for an RO membrane is higher than that of NF membranes. Recently, some commercial membranes with a salt rejection rate of above 99% have been manufactured. Such membranes are used for desalinating seawater and concentrating juices.

## 5) Forward osmosis (FO) membranes\*

FO membranes show removal performance equivalent to those of NF and RO membranes. A RO membrane allows the process liquid to pass from the solution with the higher concentration to that with the lower concentration. However, with an FO membrane, the direction of the process liquid flow is reversed. It also differs from RO membranes in that the process liquid is transferred using osmosis instead of pressure generated by a pump. Unlike the other four previously mentioned water treatment membranes, FO membranes are currently undergoing the research and development (R&D) or verification stage, and are yet to undergo large-scale commercialization (\*FO membranes are not defined by IUPAC; this definition was provided by the author).



Figure I.4 Types of water treatment membranes.

#### I.2.3. Technology changes in reverse osmosis (RO) technology

Of the above-described water treatment membranes, RO membranes have contributed significantly to the advancement of water treatment technologies, seawater desalination, and wastewater recovery as they are able to separate salts from water. They have also contributed to improving the effective use of water resources. Presently, RO membranes are the mainstream technology for seawater desalination; they have replaced the previously used distillation method. Notwithstanding the monopoly of RO membranes in desalination today, the change from distillation to membrane technology was difficult in terms of the desalination cost (\$/m³ of treated water).

Up to the 1990s, desalination technology (exemplified by seawater desalination) was used in unique environments only, namely areas that were economically wealthy yet suffered from extreme water shortages, such as oil producing countries, and when the requirement for treated water is essential, such as ultrapure water used in the electronics manufacturing industry. At the time, the cost of desalinated water amounted to several dollars per cubic meter, and lowering this price was the key challenge. The decrease in the cost of desalinated water with RO membrane technology can be attributed to two reasons.

#### 1) Improvement in water recovery rate

Improving the ratio of treated water produced from raw water (e.g., seawater) can reduce the costs of water intake, pretreatment equipment, and associated reagents. Since the discharge from high-pressure pumps (which require pressure higher than osmotic pressure) can also be reduced, the power consumption decreases.

For standard seawater with NaCl concentrations of 3.5 wt%, the water recovery rate of the RO membrane was initially ca. 40%; however, in recent years, the development of multi-stage RO membranes splits the process into two stages, and thus, RO membranes that can handle extremely high pressure and achieve a water recovery rate of 60% have been developed. On the other hand,

improvements in the recovery rate are accompanied by an increase in the salt concentration on the surface of the membrane, leading to higher osmotic pressure and the need for extremely high filtering pressure, which create the need for resistance to the high pressure. Moreover, it becomes necessary to add scale inhibitors to suppress precipitation.

#### 2) Advancements in energy recovery technologies

Raw water passes through RO membranes at high pressures of 6–8 MPa to provide desalinated water. The pressurized raw water that remains after obtaining the desalinated water was initially released. In recent years, this pressurized energy has been tapped by energy recovery devices (such as turbines), thereby facilitating the recovery of electric energy necessary for the RO membrane process. Energy recovery that uses a pressure conversion energy recovery device is especially efficient as it allows for the recovery of 60–90% of the released energy [9].



Figure I.5 Changes in the cost of producing desalinated water over time [10].



Figure I.6 Breakdown of OPEX and CAPEX for RO membrane seawater desalination plant [11].

Figure I.5 summarizes the changes in desalination cost of water over the years using RO membrane technology [10]. Initially, this cost amounted to several dollars per cubic meter. However, the performance improvements of RO membranes, progress in energy recovery technologies, and mass production, as described above, have helped reduce the desalination cost to just under \$1/m3 in recent years and to as low as \$0.5–0.7/m3 at the latest large-scale facilities.

Figure I.6 shows the breakdown of operating expenditure (OPEX) and capital expenditure (CAPEX) at a recently built RO membrane seawater desalination plant [11]. Focusing on OPEX shows that depreciation and the cost of electricity each constitute one-third of the total expenditure. The cost of electricity is derived from the electrical energy used to power the high-pressure pump. This cost continues to remain high even today despite the use of energy recovery devices. As this cost is essential (given that the RO membrane uses pressure as the driving force), there is little room to reduce its use. Depreciation cost is calculated as CAPEX divided by the amortization period; thus, this

cost can be discussed in terms of the structure of CAPEX. About 60% of CAPEX can be attributed to pretreatment membrane devices, high- and low-pressure RO membrane devices, power recovery devices, and ion-exchange resins. Theoretically, it is possible to lower the costs of these devices by improving the water recovery rate; however, such improvement is already at its theoretical limit, given the balance that must be maintained between the RO membrane resistance design (maximum: 80–100 bar) and osmotic pressure.

Thus, viewing the technological changes of RO membranes and the fluctuations in the desalination cost from this perspective, the lowering of desalination costs due to continuous RO membrane technological innovations is approaching its limit and is unlikely to undergo further dramatic reduction in the future.

# I.3. Forward osmosis (FO) technology

#### I.3.1. Advantages of FO technology compared with RO technology

The concept of FO membrane separation is shown in Figure I.7. In the case of the RO membranes we have discussed above, pressure higher than osmotic pressure is applied to raw water with salt, such as seawater and wastewater, making raw water migrate to the side containing the treated water. In contrast, the FO membrane allows the draw solution (DS), which has higher osmotic pressure, to come into contact with the raw water through a semi-permeable membrane. Thus, water extraction is driven by the natural difference in the osmotic pressure between the raw water and the DS. While the RO membrane requires pressure for this task, the FO membrane uses the osmotic pressure of water, and this fact constitutes the major difference between the two membranes.



Figure I.7 Principles driving the functioning of the RO membrane and the FO membrane.

The schematic of the FO membrane system is presented (Figure 1.8). This system consists of the FO membrane, DS, and DS recycling device. Supplied raw water, such as seawater, comes in contact with the DS, which is characterized by higher osmotic pressure, through the FO membrane (the semi-permeable membrane that allows only water to pass through). The osmotic pressure difference causes the water to migrate to the side with the DS, thus diluting the DS. The diluted DS is separated and recycled into concentrated DS and pure water by the DS recycling device. Various methods have been proposed to separate and recycle the DS [12], but we present a thermal separation/recycling method as the representative case here. The DS uses macromolecular polymers whose affinity to water changes depending on the temperature. It is designed such that when the a certain temperature is exceeded, the affinity of the DS for water decreases, and phase separation into water and DS occurs. This water phase is recovered as pure water, while the DS phase is recycled as DS. Repeating this cycle separates the water from the raw water. Since the DS must be maintained at high osmotic pressure to ensure a high driving force, it is desirable that the diluted DS be separated and recycled under low-energy conditions [13].



Figure I.8 Schematic of the FO membrane system.

The advantages of FO membranes over RO membranes are summarized below.

# 1) <u>High water recovery rate</u>

Seawater desalination using RO membranes can achieve a water recovery rate of 60%. This value cannot be increased as concentrating the raw water entails an increase in its osmotic pressure, complicating efforts to apply a pump pressure higher than the osmotic pressure. Presently, commercially available RO membranes allow a maximum pressure of 8–10 MPa, which is considered extremely high; yet, concentrating raw water with osmotic pressure exceeding these numbers is impossible in principle.

On the other hand, for example, if inorganic salt at a low concentration of 5 M is used as the DS for the FO membrane, an osmotic pressure of 30–100 MPa can be achieved. This allows for a higher degree of concentration than that possible with the RO membrane without a high-pressure pump.

#### 2) Lower pressure resistance

As discussed above, the pressure for an RO membrane is supplied by a pump, the maximum value being 8–10 MPa. Therefore, RO membrane system designs require sufficient pressure resistance. In addition, the system cost rises with a high-pressure pump, given the pressure-resistant specifications of the pipe for the pressurized raw water and the remainder of the equipment. Not only is the equipment expensive, it also tends to occupy a considerable amount of space.

In contrast, the FO membrane uses osmotic pressure as the driving force; thus, the FO membrane does not require a pressure-resistant design. High-pressure pumps, pressure-resistant pipes, and other such equipment become unnecessary as well.

#### 3) <u>Reduced anti-corrosion measures</u>

Since the RO membrane requires high pressure resistance, the pipes and other equipment are made of metal (primarily stainless steel). RO membrane-treated water is highly corrosive for metal; thus, anti-corrosion measures must be taken with degassing treatment, such as the removal of dissolved oxygen and carbon dioxide.

In contrast, the FO membrane does not require pressure resistance for pipes and equipment; thus, plastic can be used. This negates the need for anti-corrosion measures.

#### 4) Lower electricity cost

One-third of the desalination cost in RO membrane systems is attributed to electricity for the high-pressure pump supplying the high pressure to the raw water (Figure I.6).

FO membrane systems, in contrast, do not require a high-pressure pump; thus, the decrease in the cost of electricity is notable.

#### 5) <u>Reduced pretreatment cost</u>

Continuous filtering with the RO membrane reduces system performance due to membrane fouling. Therefore, as a pretreatment, raw water purified with a UF membrane and reagents must be used to clean the RO membrane and suppress fouling. This pretreatment comprises 20% of the initial cost (Figure I.6).

However, with the FO membrane, the water migrates without added pressure; thus, membrane fouling does not occur as easily even when the same permeation performance is achieved and simpler pretreatment is expected.

The differences in water treatment technologies using FO and RO membranes are summarized in Table I.1. The FO membrane shows a higher water recovery rate, requires a less stringent pressure-resistant design and anti-corrosion measures, and reduces the costs of electricity and pretreatment considerably. In addition, it might be possible to extract water and organic components from highly concentrated salt solutions and raw water, respectively, with an FO membrane; both solutions are difficult to treat with RO membranes. Moreover, the FO membrane is expected to become cheaper and more efficient as a water treatment technology than the conventional technologies applied today.

Characteristics	RO membrane	FO membrane	
1) Water recovery rate	Cannnot exceed 60%	Higher than the RO membrane (the upper limit of concentration is considerably higher)	
2) Pressure-resistant design	Necessary	Unnecessary	
3) Anti-corrosion measures	Necessary	Unnecessary	
4) Electricity cost	High-pressure pump required	High-pressure pump not required (a cost reduction is expected)	
5) Pretreatment	Necessary	Simpler pretreatment is expected	

Table I.1 Advantages offered by the FO membrane over the RO membrane for water treatment.

#### I.4. Remaining problems of FO membrane

#### I.4.1. Technology changes in FO membrane

A timeline showing the progress in the development of FO membrane technologies appears in Figure I.9 [14].

R&D on FO membranes began in the 1990s. This progress has developed into a heated global competition today, and the number of presentations and publications on the subject is increasing [14]. R&D on FO membrane technology began with the use of FO flat sheets composed of cellulose triacetate (CTA). CTA is used as a desalination material in RO membranes. Although it is not very permeable, it is easily workable. In the industrial sector, Hydration Technology Innovations (HTI; presently, Fluid Technology Solutions: FTS) was the first to produce FO flat sheets made of CTA, but their performance was inadequate. HTI discontinued producing FO membranes after being taken over by FTS. Since adequate water permeability cannot be achieved with CTA, it shifted to the development of a thin film composite (TFC) membrane that uses polyamide with superior water permeability.

The polyamide TFC-FO flat sheet (namely a thin film composite of polyamide on a flat support layer) became the mainstream polyamide-containing FO membrane with separate separation and functional layers. The polyamide TFC-FO flat sheet is the mainstream technology in present-day RO membrane manufacturing as it is suited to mass production. However, it has not achieved high enough performance for commercialization. In order to improve performance, a TFC-FO flat sheet is being competitively developed. In recent years, the TFC-FO flat sheet has been transformed into a hollow fiber. By processing it in this new shape, the area of the membrane per unit volume has been increased over that of a flat sheet; thus, further performance improvement is expected for actual module products. However, though hollow fiber TFC-FO membranes are easy to manufacture in laboratories, mass production is a challenge. In addition, despite the improved performance with the hollow fiber shape, the performance of FO membranes needs further improvement, and thus, their practical use is not possible. Therefore, FO membrane systems are not used commercially at this time.



Figure I.9 Timeline showing the progress in the technological development of the FO membrane [14].

#### I.4.2. Thin Film composite FO membrane

Figure I.10 summarizes the interfacial polymerization method used to manufacture TFC-FO membranes and the structure [15]. Aromatic polyamides, which serve as the active layer, are polymerized onto the porous substrate or the support layer. The active layer has an affinity to water molecules, allowing selective permeation of water by removing ions such as Na and Cl. The support layer, as the name suggests, is used only to physically support the aromatic polyamide. In general, in terms of material and specification requirements, the aromatic polyamide should be easily formed and physical strength adequate for practical use should be maintained. The active layer is usually created by applying the interfacial polymerization method on top of the support layer to provide a thickness of several tens to hundreds of nanometers. Figure I.10 shows the schematic of the interfacial polymerization method for the aromatic polyamides. The aromatic polyamide is polymerized as a thin film, as the amine and acid halide react at the interface between the aromatic amine and aromatic acid halide organic solvent solutions. As this polymerization reaction occurs on the surface of the support layer, polyamides are formed at the surface of this layer.



Interfacial polymerization of aromatic polyamide



Figure I.10 TFC membrane structure and interfacial polymerization method [15]

## I.4.3. To produce high performance FO membrane

The FO membrane differs from the RO membrane in that the latter uses pressure as the driving force, whereas the FO membrane uses the osmotic pressure difference between the raw water and DS that are in contact as the driving force. However, the FO membrane suffers from a unique problem, namely internal concentration polarization (ICP). Let us explain ICP with an example in which the raw water (feed solution: FS) lies on the side with the polyamide active layer and the DS lies on the support layer's side (active layer facing the feed solution: AL-FS; Figure I.11).

As shown in Figure I.11, ICP is a phenomenon in which the DS concentration gradient occurs in the support layer. Since the FO membrane uses the osmotic pressure difference between the DS and raw water as the driving force, theoretically, this pressure difference between the raw water and DS  $(\Delta \pi)$  serves as the driving force, allowing for water permeability relative to the osmotic pressure difference. However, during actual operation, water migrates from the side containing the raw water to that with the DS through the active layer; thus, the DS concentration closest to the polyamide active layer is diluted by the migrated water, reducing the effective osmotic pressure difference  $(\Delta \pi_c)$ to below  $\Delta \pi$ . To regulate such a decrease in the effective osmotic pressure, the support layer structure must allow fresh DS to constantly enter the support layer as well as quickly disperse and replace the diluted DS near the active layer. However, none of the available FO membranes can sufficiently regulate ICP, which thus continues to remain the biggest challenge in the performance improvement of FO membranes [16]. The relationship between the water permeability flux and DS concentration for an HTI-manufactured FO membrane are shown in reference [17]. Theoretically, the water permeability flux is positively proportional to the osmotic pressure difference (synonymous to the DS concentration), as shown by the theoretical value (solid line), but in reality, the impact of ICP leads to a different value from the theoretical at higher concentrations.



Figure I.11 ICP schematic diagram.

The structural parameter is used as an index to evaluate the likelihood of ICP occurring in the support layer of the FO membrane (see Equation (I.1)) [16, 17]. The smaller the value of S, the better. The S value depends on the curvature  $\tau$ , porosity  $\varepsilon$ , and membrane thickness t. With regard to the curvature, linear and larger support layer pores are preferable. In terms of porosity, the porosity of the support layer should be preferably high, and the structure should have many pores. In addition, as regards membrane thickness, the thinner the support layer, the better. In other words, a support layer that is thinner and more porous, and is characterized by a linear pore structure provides higher water permeability for the TFC-FO membrane.

$$S = \frac{\tau t}{s}$$
 (Equation I.1)

#### **I.5.**Purpose of this study

Polyvinylidene difluoride (PVDF) is a crystalline polymer with high crystallinity and a stable crystalline structure. Moreover, since the glass transition temperature is low (-35 to 40°C), it exhibits good strength, flexibility, and chemical resistance at room temperature [18]. Therefore, it has been actively researched since the 1980s and serves a central material in currently used hollow fiber water treatment membranes, such as MF and UF membranes [19, 20]. As a water treatment membrane, PVDF is a relatively new material, but many studies have applied it as hollow fiber membrane for water treatment (e.g., to regulate pore structure [21, 22] and produce hydrophobic or hydrophilic PVDF [23]).

Many studies have reported using materials such as polysulfones [24], polyethersulfones [25],

polyacrylonitrile [26], and polyketones [27] as the support layer of the hollow fiber in polyamide interfacial polymerization of TFC-FO membranes. However, studies on FO membranes using PVDF, the mainstream support layer material in hollow fiber UF and MF membranes are limited to flat sheets [28] and nanofibers [29]; none of them focus on the hollow fiber type.

In the present study, we explored the pore regulation and hydrophilicity technologies to prepare hollow fiber membranes using PVDF, which provides the necessary balance between sufficient strength for forward osmosis and the ICP regulating function. Subsequently, we prepared a TFC-FO membrane that interfacially polymerizes polyamide with the PVDF hollow fiber membrane as the base, and we evaluated its performance. In addition, based on the results of this performance evaluation, we conducted a business strategy study to commercialize hollow fiber FO membranes made of PVDF. Thus, we aim to establish a manufacturing technology for TFC-FO hollow fibers made of PVDF and propose a business strategy for its commercialization.

#### I.6.Scope of this thesis

**Chapter I** contained the history of water treatment technology was organized and the technological transition of FO membranes was investigated. As a results, it was shown that FO membrane in which polyamide is interfacial polymerized on the porous hollow fiber support layer that can suppress ICP is most likely to improve the FO performance.

**Chapter II** discussed PVDF/ε-caprolactone/polymeric additive systems to clarify the functions of the polymeric additives, polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) in the thermally induced phase separation process to control pore structure of PVDF porous support membrane. In this study, we clarified the functions of PEG and PVP in phase separation process. We also clarified that the phase structure of PVDF membrane can be controlled by selection of the polymeric additives.

**Chapter III** studied a method to prepare the hydrophilized PVDF hollow fiber support membranes named the polyvinyl alcohol (PVA) diffusion method. In this method, the entire PVDF hollow fiber membrane can be hydrophilic by diffusing PVA frome the bore side to the outer surface of PVDF hollow fiber membrane. Using this method, PVA hydrophilized PVDF hollow fiber membrane support and not hydrophilized (hydrophobic) PVDF hollow fiber membrane support were prepared. In this study, polyamide was interfacial polymerized on these hollow fiber membrane supports to fabricate the polyamide PVDF thin film composite membranes, and the effects of the structure and hydrophilicity of the support layer on RO and FO performance were evaluated.

**Chapter IV** studied a new PVDF hollow fiber membrane fabrication technology named HTR-NIPS method. As a result of investigating the conditions to fabricate the PVDF hollow fiber membrane support having a large bicontinuous pore structure using HTR-NIPS method, it was clarified that the following two conditions were satisfied; (1) the stock solution does not have a gelation temperature, (2) the coagulation temperature is higher than the stock solution of upper critical solution temperature (UCST). Using the stock solution (PVDF/ $\gamma$ -butyrolactone/PVP system) satisfying these conditions, we succeeded to produce the PVDF hollow fiber support having a large bicontinuous structure. The polyamide active layer was interfacial polymerized on this PVDF hollow fiber supports as forward osmosis membrane, and these FO membrane performance was evaluated.

**Chapter V** investigated the zero liquid discharge (ZLD) system using FO membrane in the ZLD market. In order to provide value to the ZLD system using FO membrane, it is important to provide economic value to ZLD water treatment costs. It was revealed that FO membranes can gain competitiveness in the ZLD market if they can be manufactured on a scale comparable to RO mambranes.

Chapter VI summarized the conclusions of this thesis.

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# Chapter II Principle of phase separation structure control technology for porous PVDF support layer

## **II.1. Introduction**

In order to improve the performance of the FO membrane by suppressing ICP, it is necessary to understand the principle of controlling porous structure of PVDF support layer. Therefore, in this section, in order to understand the principle of controlling the phase separation structure of the PVDF support layer, we focused on the phase diagram of the phase separation process.

A thermally induced phase separation (TIPS) method is employed for the industrial manufacture of ultrafiltration (UF) and microfiltration (MF) water treatment membranes. The TIPS method cools uniform polymer solutions and lowers the compatibility of polymers and solvents, thereby promoting phase separation and forming a porous structure [1]. It is an important manufacturing method for water treatment membranes using poly(vinylidene difluioride) (PVDF), which exhibits superior mechanical strength and chemical resistance.

When manufacturing porous membranes (such as those used for water treatment), it is important to analyze the phase equilibrium to regulate its pore structure. Phase separation using the TIPS method is roughly divided into the liquid–liquid (L–L) [2] and solid–liquid (S–L) [3] types. L–L separation occurs phase separation in liquid state before crystallization of the polymer, whereas the crystallization of the polymer occur first in the S–L types. The selection of the phase separation process is based on the polymer, solvent, and compositions of raw solution (including additives) used for membrane manufacturing, leading to unique phase structures. Polymer additives such as poly(ethylene glycol) (PEG) and poly(vinyl pyrrolidone) (PVP) are most commonly used to control the phase separation process of PVDF [4, 5]. Various kind of PVDF membranes are being studied using these additives [6-10].

These two additives have different and unique phase structures, but no studies have focused on the mechanisms of how these additives impact the phase equilibrium of PVDF and express unique phase structures. In addition to PVDF, these additives are also frequently used to control the phase structures of amorphous polymers such as Poly(sulfone) [11-13], Poly(ether sulfone) [14, 15], and the effects to phase separation of these additives have been studied. However, PVDF, which is a crystalline polymer, requires a mechanism analysis that takes into account the phase structure change due to crystallization. Since phase separation in PVDF was a more complex system than amorphous polymers, it was difficult to analyze.

Figure II.1 shows typical phase equilibrium generated by the TIPS method for crystalline polymers [17, 18], including PVDF. Figure II.1(a) is a phase diagram for L–L phase separation. The polymer solution dissolved at the temperature of the one-phase state is cooled below the upper critical solution temperature (UCST), thereby reaching a two-phase state. Once its temperature falls below the crystallization temperature  $T_c$ , it becomes solidified and the phase structure can be determined. In the case of L–L phase separation, UCST is higher than  $T_c$  during the cooling process; thus, the phase separation progresses in the solution state, which gives the process its name (L–L type). Figure II.1(b) shows the phase diagram for S–L phase separation. In this case, UCST is lower than  $T_c$ ; thus, the polymer solution dissolved at the temperature of the one-phase state experiences crystallization before phase separation occurs, thereby determining the phase structure. Thus, this type of separation is called S–L type separation. A lower critical solution temperature might be observed depending on the composition of the raw solution used for membrane manufacturing.



Figure II.1 Phase diagram in TIPS process; (a) L-L type, (b) S-L type.

In this study, we discuss the impact and mechanism of PEG and PVP, polymer additives that are most commonly used in the TIPS method with PVDF, on phase structure determination.

# **II.2.** Experimental

## **II.2.1.** Materials

PVDF: Solef 6013 (Solvay S.A.), PEG: Alkox L-6 (Meisei Chemical Works, ltd.), PVP: Sokalan K-90P (BASF co. ltd.) were used as raw materials and ε-caprolactone (ECL) (Fujifilm Wako pure chemical co. ltd.) was use as solvent.

# **II.2.2. Measurement methods for LCST and UCST**

The temperature of the polymer solution with one uniform phase dissolved at 120°C is lowered or increased in increments of 3°C to measure the phase separation temperature (UCST and LCST) by visually confirming the cloudiness caused by the phase separation.

# **II.2.3.** Measurement methods for crystallization temperature

PVDF is reported to go through a rapid increase in the solution viscosity (gelation) as

crystallization progresses [8, 19]. In the present study, using dynamic viscoelasticity measurements with a rotary rheometer (ARES, TA Instruments Inc.), we set the gelation temperature as T<sub>c</sub>. Specifically, the uniform, one-phase polymer solution was cooled in 5°C intervals from 120°C, and the kinematic viscoelasticity was measured at a frequency  $\omega = 0.1-100$  rad/s. As shown in Figure II.2, in the liquid state,  $\omega$  and storage modulus G' have a linear relationship. After gelation, however, a flattening of the G' curve (solid state characteristics) was observed. This point was recorded as T<sub>c</sub>.



Figure II.2 Dynamic viscoelasticity measurement of frequency dependence of PVDF.

# **II.2.4.** Preparation method for the surface structure observation sample

The polymer solution with one uniform phase that was dissolved and de-aerated at 120°C was cast on a board as 150~200 µm film and solidified in a solution at 75°C. After drying, the cast membrane surface structure was observed using a scanning electron microscope (S-300N, Hitachi co.ltd.).

#### **II.3.** Results and discussion

# **II.3.1.** Effect of PEG as polymeric additive in phase separation process

To assess the impact of PEG as an additive, we prepared a raw solution of a three-component system consisting of PVDF/ECL/PEG, where the ratio of the additive (PEG) was changed (Table II.1; see entries 1-3). We measured LCST, UCST, and T<sub>c</sub> for each solution (Figure II.3).

As the ratio of PEG relative to PVDF increased, LCST decreased and UCST increased. When the ratio of PEG was increased, the affinity of the mixture of ECL/PEG to PVDF decreased; thus, the temperature range of one phase became narrower, thereby increasing the temperature range for two phases. Similarly, T<sub>c</sub> increased as the ratio of PEG was increased. This is because as PEG increased, the affinity of the mixture of ECL/PEG to PVDF decreased, which led to the crystallization of PVDF. For all compositions, UCST was higher than T<sub>c</sub>. Thus, phase separation performed with the TIPS method for the present compositions led to an S–L type of phase separation becoming the dominating feature, causing the crystallization of PVDF to occur.

ontrios	PVDF	ECL	PEG	PVP	additive/PVDF <sup>*1</sup>	PVP in additive <sup>*2</sup>
chures	[wt%]	[wt%]	[wt%]	[wt%]	[-]	[-]
1	30	58.3	11.7	0	0.39	0.00
2	30	56.7	13.3	0	0.44	0.00
3	30	53.9	16.2	0	0.54	0.00
4	30	56.7	10.7	2.6	0.44	0.20
5	30	56.7	6.7	6.7	0.44	0.50

Table II.1 Composition of PVDF/additive systems.

\*1 Calculated by ([PEG]+[PVP])/[PVDF]

\*2 Calculated by [PVP]/([PEG]+[PVP])



Figure II.3 Phase diagram of PVDF/ECL/PEG systems.

# **II.3.2.** Effect of PVP as polymeric additive in phase separation process

Next, to assess the impact of PVP as an additive, we used a constant ratio of PVDF to the additive (0.44) and prepared a raw solution in which the ratio of PVP within the additive was varied (Table II.1; see entries 2, 4, and 5). We measured LCST, UCST, and T<sub>c</sub> for these raw dope samples (Figure II.4).

As the ratio of PVP in the additive increased, LCST decreased and UCST increased. When PVP was compared to PEG for the present composition, PVP further decreased the affinity of the mixture of ECL/PEG/PVP to PVDF. In fact, the distance (Ra) between PVDF and additives on Hansen solubility parameters (HSPs) [20] of PVP were very different from those of PVDF compared with PEG, indicating that the affinity to PVDF was lower than that of PEG (Table II.2). However, the HSPs of a polymer compound cannot be generalized due to the molecular weight and branching of the main chain; thus, the above-mentioned values serve as a reference only. Additionally, the solubility of PEG and PVP used in this study in water (used for coagulation bath as non-solvent of PVDF) was investigated. These results are summarized in Figure II.5. In the case of 5 wt% aqueous
solutions, a slight cloud point was observed in PEG at high temperature (in 90 °C), but PVP maintained a transparent solution state. It is known that a polyether-based nonionic surfactant such as PEG loses its solubility in water in high temperature [21, 22]. As described above, since PEG has a reduced solubility in water, especially when heated, it is considered that the affinity of PEG with PVDF is relatively high as compared with PVP. This is also consistent with the HSP distance analysis results.

When the amount of PVP in the additive was increased, unlike the case of PEG, UCST increased while  $T_c$  decreased. When the affinity of the raw dope to PVDF decreased, the crystallization of PVDF was promoted; thus,  $T_c$  tended to increase normally, but PVP exhibited the opposite behavior.



Figure II.4 Phase diagram of PVDF/ECL/PEG/ PVP systems



Figure II.5 Solubility in water of PEG and PVP

Table II.2 Hansen solubility parameter of polymers

Polymers	$\delta_{ m d}$ (MPa) <sup>1/2</sup>	$\delta_{ m p} \ ({ m MPa})^{1/2}$	$\delta_{ m h} \ ({ m MPa})^{1/2}$	$\mathrm{Ra}^{*1}$ $\mathrm{(MPa)}^{1/2}$	Ref.
PVDF	17.2	12.5	9.2	-	[23]
PVP	21.4	11.6	21.6	15.0	[23]
PEG	17.0	10.7	8.9	1.9	[24]

<sup>\*1</sup> Ra means the distance between PVDF and additives on Hansen parameters, calculated by

Ra between 1 and 2 =  $(4(\delta_{d1}-\delta_{d2})^2+(\delta_{p1}-\delta_{p2})^2+(\delta_{h1}-\delta_{h2})^2)^{1/2}$ 

Chen et al. [25] reported that when preparing the cast film with PVDF, the ratio of PVP in the additive increased and the crystallinity of PVDF observed in the x-ray diffraction of the cast film decreased. They confirmed by infrared spectroscopy that there is a hydrogen bonding between PVDF and PVP. They reported that the crystallinity of PVDF decreases when PVP was added because of the hydrogen bonding in Figure II.6. In addition, Cha et al. [26] reported a similar phenomenon with the hollow fiber. In our past study [8], we reported that the addition of PVP eliminated the phenomenon of viscosity increase due to PVDF crystallization. On the other

hand, we also reported that the addition of PEG promotes the phenomenon of viscosity increase due to crystallization of PVDF. We also reported that when hollow fiber membranes were fabricated by PEG added stock solution system, hollow fiber membranes having a spherulite structure as a main structure were formed by crystallization. On the other hand, we reported that the spherulite structure is no longer observed by PVP added stock solution system. From these facts, it is reasonable to think that PVP, unlike PEG, has a function of suppressing the increase in viscosity due to the crystallization of PVDF.

These PVDF crystallization suppression effects of PVP are believed to lead to a decrease in  $T_c$  despite the increase in UCST in the present composition. Here, adding PVP caused UCST to exceed  $T_c$ ; thus, phase separation took place before crystallization of PVDF, leading to the L–L type of phase separation, where the phase separation progresses in a solution state.



Figure II.6 Hydrogen bonding of PVDF and PVP

# II.3.3. Surface structure of cast film

As discussed, the present assessment system showed that additives such as PEG and PVP change

the phase separation processes of PVDF in the TIPS method. Specifically, only PEG is used as the additive and  $T_c$  exceeds UCST; thus, the S–L type of phase separation dominates. However, by adding PVP,  $T_c$  decreases and becomes lower than UCST; thus, the L–L type of phase separation dominates. In this section, we used entries 1–5 of Table III.1 to prepare a cast membrane, observed the surface structures, and assess the impact on actual membrane structures. For all compositions, the melting point of the raw dope was 120°C with one phase. We designed an assessment system such that cooling with a 75 °C bath lowered the temperature below UCST and  $T_c$ , and the phase separation and crystallization processes in the TIPS method progressed.

Figure II.7 shows the surface structure of the cast membranes (entries 1–3). In this system, if the amount of added PEG is increased,  $T_c$  and UCST both increase on the phase diagram (Figure II.3), indicating that the S–L type of phase separation is dominant. When we actually prepared a cast membrane and observed its surface structure, we found that as the amount of PEG is increased, the surface numbers of pore of the membrane decreased; thus, we discovered that a structure formed with the relatively large pore structures. Since  $T_c$  was higher than UCST, when viscosity increased with crystallization, phase separation progressed in a high-viscosity state. In addition, we observed not only pore structures but also spherulitic structures derived from crystallization on the surface of the membrane marked as entry 3; this indicated the S–L type of phase separation, where crystallization occurs first, as predicted. Entries 1 and 2 were also similar, with the S–L type of phase separation dominating. Since the temperature difference between  $T_c$  and UCST was small, however, the structures were not as prominent as in entry 3.



Figure II.7 Surface structure of PVDF membranes with different PEG content.

Figure II.8 shows the surface structure of the cast membranes for entries 2, 4, and 5. In this system, we used a constant ratio of additive to PVDF (0.44) but changed the ratio of PVP to PEG in the additive. When the PVP ratio was increased, the phase diagram (Figure II.4) showed an increase in UCST but a decrease in  $T_c$ ; thus, UCST and  $T_c$  were reversed, indicating that the L–L type of phase separation was dominant. We prepared cast membranes and observed their surface structures. An increase in the amount of PVP was accompanied by an increase in the surface numbers of pore of the membrane. A large number of fine pores tended to form compared to when only PEG was used. Since UCST exceeded  $T_c$ , the phase separation progressed in a low-viscosity solution. This led to the formation of a large number of small pores, subsequently leading to an increase in the kinematic viscosity by reaching  $T_c$  after that decided the structure.



Fig. II.8 Surface structure of PVDF membranes with different PVP content

A clear difference exists in membrane surface structures containing PEG alone and those with added PVP. This difference is determined by which type of phase separation dominates, S–L or L–L. Thus, the phase separation structure can be controlled by the selection of polymer additives.

Membrane manufacturing technologies use PVDF, PEG, and PVP most frequently as polymer additives. Various membranes have been studied and manufactured using these additives. However, not many studies have explored the theoretical fundamentals of membrane pore structures. The system examined in the present study provided a detailed explanation of the difference between phases and membrane structures containing PEG and PVP. The target membrane structure varies based on the use and objective. The performance does not depend on the superiority of a particular additive; the phase structure must be understood and controlled in order to improve membrane manufacturing technology.

# **II.4. Summary**

In the present study, we explored the function of the most commonly used materials, PEG and PVP, in various polymer membrane manufacturing technologies including PVDF. We assessed a PVDF/ECL/additive system to study the TIPS method.

We measured LCST, UCST, and T<sub>c</sub> and prepared a phase diagram after changing the amounts of additives PEG and PVP. The results revealed the following properties of PEG and PVP.

# (a) PEG

• Reduces the affinity of the mixture of ECL/PEG to PVDF, narrowing the temperature range for the one-phase state.

• When UCST increases with the addition of PEG, T<sub>c</sub> also increases.

• The S–L type of phase separation is dominant.

# (b) PVP

• Reduces the affinity of the mixture of ECL/PEG/PVP to PVDF, narrowing the temperature range for the one-phase state.

- UCST increases with the addition of PVP, but  $T_c$  decreases.

• The L–L type of phase separation is dominant.

As such, the present study clarified the mechanisms of the polymer additives PEG and PVP in the TIPS method and showed that the phase separation structure of PVDF can be regulated by the selection of polymer additive.

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# Chapter III Preparation of FO membrane with high strength and hydrophilic PVDF hollow fiber membrane support

# **III.1. Introduction**

In order to put the FO membrane with PVDF support into practical use, sufficient strength and a technology for making PVDF hydrophilic to suppress ICP are required. In this section, a high strength PVDF hollow fiber membrane support was prepared by using the phase separation technology. Furthermore, we developed a technology to make PVDF hydrophilic named polyvinyl alcohol (PVA) diffusion method. Polyamide was interfacial polymerized on the PVDF support utilizing these methods, and its FO performance was evaluated.

Currently, the reverse osmosis (RO) process, which is mainstream desalination technology, requires pressurization from a high-pressure pump as a driving force, whereas the forward osmosis (FO) process doesn't require pressurization for the driving force [1-4]. The development of a high-performance desalination membrane and mass-production technology is necessary for the commercialization of energy-saving water supply systems such as the FO process [5, 6].

A thin-film composite (TFC) membrane consists of an aromatic polyamide (PA) active layer formed on a support membrane via interfacial polymerization [7, 8]. There are many reports of using interfacial polymerization to prepare PA-RO and PA-FO TFC flat-sheet membranes [9]. However, more research is required on hollow fiber membranes [10], which have a higher surface area, for use in large-scale modules. Research into support layer materials for hollow fiber RO and FO membranes has been conducted for a variety of materials such as polysulfone (PSf) [11], polyethersulfone (PES) [12], polyacrylonitrile (PAN) [13], and polyketone (PK) [14]. There has been no research, however, on the use of polyvinylidene fluoride (PVDF) — a material used for

mainstream UF membranes and MF membranes that require high levels of physical and chemical durability — as a support layer in hollow fiber RO and FO membranes. Research has been reported only for flat [15] and nanofiber membranes [16].

By improving the characteristics of the support membranes in the construction of a TFC-PA hollow fiber membrane, increases in physical strength and water permeability may be achieved in the future, for high performance membrane development and mass production of membranes. Previous studies have suggested that the hydrophilicity of the support membrane could play an important role in the formation of PA via interfacial polymerization reactions and the suppression of internal concentration polarization (ICP) [17-25]. Gains in the physical strength and water permeability of FO membranes are expected with the development of PVDF support membranes. PVDF, however, is a hydrophobic material. Thus, coating PVDF with a hydrophilic polymer to increase hydrophilicity is one method for the preparation of high-performance RO and FO membranes. Park et al. have reported PVDF nanofibers coated with polyvinylalchohol (PVA), a hydrophilic polymer, to prepare a flat TFC membrane [26]. The PVA coating suppressed the ICP, and a high-performance FO membrane was obtained. The Park study used only flat membranes, however, and no report of hollow fiber membranes could be found in the literature.

In the present study, we prepared PA TFC hollow fiber membranes by interfacial polymerization on high-strength PVDF support membranes via a thermally induced phase separation (TIPS) method. In order to reduce the ICP of the support membrane, the PVDF hollow fiber membranes were coated with PVA via the diffusion of bore fluid to the outer surface of membranes. For reference, a PA TFC hollow fiber membrane fabricated on a PSf support via nonsolvent induced phase separation (NIPS) was investigated. The hydrophilicity of the support membranes was investigated for the effect on RO and FO membrane performance.

#### **III.2.** Experimental

## **III.2.1.** Materials and chemicals

The PVDF and PSf used in the preparation of the suppor hollow fiber membranes was Solef 6010 (Solvay Co., Brussels, Belgium) and Ultrason S3010 (BASF Co., Ludwigshafen, Germany), respectively. PVA (PVA-205, purity >94.0%, Kuraray Co., Tokyo, Japan) was used to coat the membranes. Silica particles (Aerosil 50, Nippon Aerosil Co., Tokyo, Japan) were used as a pore-forming additive. Gamma-Butyrolactone (GBL, purity >99.0%), N,N-dimethylformamide (DMF, purity >99.0%), N,N-dimethylacetamide (DMAc, purity >98.0%), Glycerine (Gly, purity >99.5%), polyethylene glycol (PEG 200, PEG 600), sodium hydroxide (NaOH, purity >97.0%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, purity >95.0%), glutaraldehyde (24.0~26.0% aqueous solution), and sodium sulfate (purity >99.0%) were purchased from Fujifilm Wako Pure Chemical Co. (Osaka, Japan).

The reagents used for interfacial polymerization were m-phenylenediamine (MPD, purity >95.0%), triethylamine (TEA, purity >99.0%), 10-camphorsulforic acid (CSA, purity >98.0%), sodium dodecyl sulfate (SDS, purity >95.0%), hexamethylphosphoric triamide (HMPA, purity >97.0%), 1,3,5-benzentricarbonyl trichloride (TMC, purity >98.0%), and n-hexane (purity >99.0%). These reagents were purchased from Fujifilm Wako Pure Chemical Co..

#### **III.2.2.** Preparation of PVDF and PSf support layers

PVDF hollow fiber support membranes were fabricated via the TIPS process. A mixture of PVDF, GBL, silica, and PEG200 (weight ratio of 34:21:25:20) was heated and mixed at 155 °C in a twin-screw extruder to prepare a stock solution for membrane fabrication. A mixture of PVA, DMAc and Gly (weight ratio of 2:58.8:39.2) was prepared and used as the bore fluid. The membrane fabrication stock solution and bore fluid were extruded into a spinneret. By extruding this mixture into an outer coagulation solution consisting of 20% aqueous sodium sulfate solution at 80 °C, a

PVDF hollow fiber membrane with an external diameter of 1,000 µm and an internal diameter of 600 µm was fabricated. Sodium sulfate was added to suppress the dissolution of solvents from the fabricated stock solution to an outer coagulation solution due to the salting-out effect that enhanced the TIPS effect. Following an elongation process, silica particles were extracted and removed in an aqueous NaOH solution. After washing and neutralizing the solution, the resultant PVDF hollow fiber membrane was washed in an 80 °C hot water bath to remove solvents and to diffuse the PVA in the bore fluid. The total amount of PVA diffused in the hot water bath was monitored using a PVA iodine blue color reaction[27] and 70% of the PVA in the bore fluid was diffused into the hot water bath. During this process, the surface of the hollow fiber membrane was coated with PVA via diffusion from the bore fluid to the outer surface of the hollow fiber membrane. Afterward, the hollow fiber membrane was immersed in an aqueous solution of sulfuric acid and glutaraldehyde to crosslink the PVA. The crosslinked PVA was not soluble in water. After washing and neutralizing the solution, it was dried. Hereafter, this membrane will be referred to as a PVA-PVDF membrane [28]. For comparison, a PVDF hollow fiber membrane also was fabricated using the bore fluid without PVA.

PSf hollow fiber membranes were fabricated via the NIPS method. PSf, DMF and PEG 600 (a weight ratio of 20:44:36) were dissolved at 80 °C to prepare a membrane fabrication stock solution. Then, both the membrane fabrication stock solution at 25 °C and a PVA, water and DMF bore fluid mixture (a weight ratio of 2:13:85) was extruded through a spinneret. The fabricated hollow fiber membrane had an external diameter of 1,000 µm and an internal diameter of 600 µm. The PVA diffusion and the crosslinking of PVA were accomplished via the same procedure described above. The PSf membrane fabricated in this method was referred to as a PVA-PSf membrane. For comparison, a PSf hollow fiber membrane was also fabricated without the use of PVA.

#### III.2.3. Interfacial polymerization on porous hollow fiber membranes

An active layer was formed on the outer surface of the hollow fiber membrane via interfacial polymerization of the MPD and TMC. The conditions for the formation of the active layer are shown in Table III.1. Both ends of the membrane's hollow fiber were sealed to prevent entry of the solutions from the bore side, and the membrane was then slowly immersed into an aqueous MPD solution for 2 minutes. Afterward, excess MPD solution was removed. Then, the membrane was slowly immersed in a TMC hexane solution for 1 minute, and interfacial polymerization was performed. Following the interfacial polymerization, the hollow fiber membrane was heat-treated for 6 minutes at 120 °C, and then washed with pure water, yielding a TFC membrane with a PA layer [14, 29].

Tabl	e III.1	Conditio	ns for	· interfacia	ıl po	lymerization
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MPD aqueous sulution				TMC-hexa	Drying				
MPD	TEA	CSA	SDS	HMPA	time	TMC	time	temp.	time
		(wt%)			(min)	(wt%)	(min)	(°)	(min)
3	1.65	3.4	0.225	1.5	2	0.15	1	120	6

# III.2.4. Membrane characterization

The surfaces and cross-sections of the hollow fiber membrane structures were observed via scanning electron microscopy (SEM; Hitachi S-300N, Hitachi Co., Tokyo, Japan). The structure of the PA active layer that was fabricated via interfacial polymerization was observed via field-emission SEM (FE-SEM; Hitachi SU-70, Hitachi Co., Tokyo, Japan). For cross-section analysis, a membrane sample was fractured in liquid nitrogen. The outer and inner diameters of the hollow fiber membranes were measured using a microscope (VHX-5000 digital microscope, Keyence Co., Tokyo, Japan). To measure the pure water permeability (PWP) of the hollow fiber membrane, a module of a

hollow fiber membrane with an effective length of 20 cm was prepared by sealing one end. The PWP  $(l/m^2/hr/bar = LMH/bar)$  was obtained based on the weight of permeated water after one minute at an external pressure of 1 bar. The PWP measurements were conducted using a hollow fiber membrane module in a completely dry state in order to obtain the PWP of a dry membrane. Then, the hollow fiber membrane module was immersed in 50% ethanol for 10 minutes, and washed with pure water for 10 minutes thus making it completely wet, at which point the PWP for the wet membrane was measured.

To obtain the diameter of the hollow fiber membrane pores, the outer surface of the hollow fiber membrane was observed using SEM. The images were then analyzed using image analysis software (Image-Pro Plus, Planetron Co., Tokyo, Japan) to obtain the pore area, which then provided the pore size distribution. XPS analysis was performed using a Quantera SXM (Ulvac-Phi Inc., Kanagawa, Japan). The total porosity (%) in the hollow fiber membrane was calculated using equation (II.1) to compare the membrane weight difference between a dry and a wet state. The infrared absorption spectra of the hollow fiber membranes were obtained by attenuated total reflection (ATR) using an infrared spectrophotometer (JIR-5500, JEOL Co., Tokyo, Japan). To establish the breaking strength, a tensile test was conducted using a 5 cm length of hollow fiber membrane stretched at a rate of 100 mm per minute in 25 °C water using an autograph (AG-Xplus, Shimadzu Co., Kyoto, Japan). The breaking strength was based on the load required to break the test piece.

$$porosity(\%) = \frac{(wet state weight(g)) - (dry state weight(g))}{wet state weight(g)} \times 100 \quad (II.1)$$

#### III.2.5. RO and FO performance measurement

A laboratory-scale experimental setup was used to measure the performance of the TFC membrane during RO and FO (Figure III.1). The test module consisted of a nylon tube with an outer diameter (O. D.) of 10 mm and an inner diameter (I. D.) of 7.5 mm and 5 hollow fiber membranes, each with an effective length of 10 cm. The experiments were performed using wet hollow fiber membranes.



Figure III.1 Schematic diagrams of RO and FO systems for measuring membrane performance

In the RO test, an aqueous NaCl solution (0.017 M, 1,000 ppm) was cross-flowed at a linear velocity of 29 cm/sec on the shell side of the membrane, and a pressure of 4 bar was applied. The RO flux ( $J_w^{RO}$ ;  $l/m^2/hr = LMH$ ) was obtained from the weight of the permeated water, the membrane surface area, and the filtration time. A 1,000 ppm NaCl rejection (Rs, %) was obtained using Equation (III.2).  $C_F$  and  $C_t$  denote the salt concentrations of the feed and permeated solution, respectively. These were obtained via electrical conductivity measurement (SC-72, Yokogawa Electronics Co., Tokyo, Japan). The water permeability coefficient, A (LMH/bar), and the salt permeability coefficient, B (LMH), were calculated using Equations (III.3) and (III.4) [30, 31]. Here,  $\Delta P$  (bar) represents the pressure difference between the feed side and the permeant side during the RO experiments. The osmotic pressure of the 0.017 M NaCl was calculated at 0.85 bar using the

Van't Hoff Equation, and was subtracted from an applied pressure of 4 bar, which resulted in a total pressure of 3.15 bar.

$$R_{\rm s} = \left(1 - \frac{C_{\rm t}}{C_{\rm F}}\right) \times 100 \quad (\text{III.2})$$
$$A = J_{\rm w}^{\rm RO} / \Delta P \quad (\text{III.3})$$
$$B = J_{\rm w}^{\rm RO} \left(\frac{1}{R_{\rm s}} - 1\right) \quad (\text{III.4})$$

For the FO test, measurements were performed for both the active layer facing the feed solution (AL-FS) mode and the active layer facing the draw solution (AL-DS) mode. For AL-FS measurement, a feed solution of 800 mL of pure water was circulated at a constant linear velocity of 29 cm/sec on the shell side of the hollow fiber membrane, and the draw solution consisted of 500 mL of a 1.0 M NaCl solution. The linear velocity for circulation at the surface on the bore side of the hollow fiber membrane was controlled to a constant 12 cm/sec. Each experiment was run continuously for 40 minutes, and then changes in the weight of the permeated water were measured after allowing it to settle for 10 to 30 minutes. Changes in the weight and electrical conductivity of the feed solution were also measured, and values were obtained for both the water  $(J_{\rm w}^{\rm FO}_{\rm (AL-FS)};$ LMH) and reverse-salt flux  $(J_s^{FO}(AL-FS); g/m^2/hr = gMH)$ . The measurements in AL-DS mode were conducted in the same manner, but the feed and the draw solutions were switched in the flow side. The feed solution (800 mL of pure water) was circulated through the bore side of the hollow fiber membrane at a constant velocity of 12 cm/sec, and the draw solution (500 mL of 1.0 M NaCl solution) was circulated on the shell side of the hollow fiber membrane at a constant linear velocity of 29 cm/sec. The values for both the water ( $J_w^{FO}_{(AL-DS)}$ ; LMH) and reverse-salt flux ( $J_s^{FO}_{(AL-DS)}$ ; gMH) were again obtained in the same manner.

The obtained A, B and  $J_{\rm w}^{\rm FO}_{\rm (AL-FS)}$  values were used to calculate the structural parameter, S, via

Equation (III.5) [15, 32]. Here, *D* is the diffusion coefficient of the draw solution (NaCl)  $(1.61 \times 10^{-9} \text{ m}^2/\text{sec})$  [31], and  $\pi_{\text{DS}}$  and  $\pi_{\text{FS}}$  are the osmotic pressures of the draw solution and the feed solution, respectively. Based on the Van't Hoff Equation, the osmotic pressure of 1.0 M of NaCl is roughly 50 bar. The structural parameter *S* (µm) was expressed as membrane thickness, *t* (µm), and tortuosity,  $\tau$  (-), divided by the porosity,  $\varepsilon$  (-), as shown in Equation (III.6).

$$J_{w}^{FO}{}_{(AL-FS)} = \frac{D}{S} \ln \left( \frac{B + A\pi_{DS}}{A\pi_{FS} + B + J_{w}^{FO}{}_{(AL-FS)}} \right)$$
(III.5)  
$$S = \frac{\tau t}{\varepsilon}$$
(III.6)

#### **III.3. Results and discussion**

#### **III.3.1.** Characterization of the support hollow fiber membranes

SEM images of the support hollow fiber membranes are shown in Figure III.2. The outer surface (5,000x), cross-section with low magnification (60x), and cross-section with high magnification (300x) are shown in Figure III.2 for both PVA-PVDF and PVA-PSf hollow fiber membranes. PVDF and PSf membranes had a pore structure similar to that of PVA-PVDF and PVA-PSf membranes, respectively. As shown in Figure III.2, the PVA-PSf membrane had larger pores than the PVA-PVDF membrane. The outer and inner diameters, the total porosity, and the average pore size of the outer surfaces of the four hollow fiber membranes (PVA-PVDF, PVDF, PVA-PSf, and PSf) are summarized in Table III.2. The outer and inner diameters were about 1,000 and 600 µm, respectively, for all hollow fiber membranes. The total porosities of PVA-PVDF and PVDF membranes were 63 and 64%, respectively, while those of PVA-PSf and PSf membranes were 78 and 76%, respectively. Thus, PVA-PVDF and PVDF membranes had the denser structures. Additionally, the pore sizes on the outer surfaces of PVA-PVDF and PVDF membranes had the denser structures. The outer surfaces are shown in Figure III.3. The PVA-PSf membrane had a broader pore distribution and also a larger average pore size than that of the PVA-PVDF membrane.



Figure III.2 SEM images of the (a) PVA-PVDF and (b) PVA-PSf hollow fiber membranes

hollow fiber mebranes	outside diameter [µm]	inside diameter [µm]	polymer ratio [wt%]	pore size [µm]	
PVA-PVDF	$995\!\pm\!16$	$594 \pm 12$	34	0.15	
PVDF	998±16	596±12	34	0.15	
PVA-PSF	$999\pm10$	$604 \pm 10$	20	0.19	
PSF	$1001\!\pm\!10$	$606\pm10$	20	0.19	

Table III.2 Characterization of the fabricated hollow fiber membranes



Figure III.3 Pore size distributions on the outside surfaces of PVA-PVDF and PVA-PSf membranes

In order to verify the hydrophilicity of the hollow fiber membranes, their water-contact angles were measured (Figure III.4). For PVA-PVDF membranes, the water-contact angle was 45.2° on the outer surface, and 40.0° on the inner surface. Both the outer and inner surfaces were hydrophilized. This indicates that PVA can diffuse from the bore fluid to the outer surface and contributes to the high hydrophilicity of both surfaces. Also, for PVA-PSf membranes, both the outer and inner surfaces were hydrophilized (46.5° and 42.4° on the outer and inner surfaces). Conversely, PVDF had a water-contact angle of 94.8° on the outer surface and 85.4° on the inner surface, which made these membrane surfaces hydrophobic. Data for the water-contact angles of PSf membranes also show that these membrane surfaces were hydrophobic (100.3° and 90.2° on the outer and inner surfaces). PVA-coated membranes showed similar water-contact angles, even after immersion in hot water (at 90 °C) overnight (Figure III.5), which confirmed that the hydrophilicity of the support membrane was stable due to PVA cross-linking.



Figure III.4 Water-contact angles on the outer and inner surfaces of four hollow fiber membranes



\* PVA coated membranes were immersed in hot (90 °C) water overnight.

Figure III.5 Comparison in water contact angles of PVA coated membranes before and after immersed in hot water (at 90 °C) overnight.

The results of XPS analysis of the hollow fiber membranes appear in Table III.3. PVA-PVDF and PVA-PSf membranes showed an increased intensity of the O1s compared with those of PVDF and PSf membranes. This increase in the intensity of the O1s was due to the PVA coating. In particular, the increase in the intensity of the O1s was more remarkable at the inner surfaces than at the outer surfaces, which indicates that PVA had diffused from the inner surfaces (bore fluid) to the outer

surfaces, which confirmed that the PVA-PVDF and PVA-PSf membranes were successfully coated with PVA.

	Manaharanaa			Atomic%		
	Memoranes	C1s	O1s	F1s	Si2p	S2p
	PVA-PVDF	54.75	7.30	37.07	0.88	-
Outer	PVDF	55.39	5.31	38.97	0.33	-
surfaces	PVA-PSF	76.94	20.90	-	0.33	1.83
	PSF	82.71	13.99	-	0.21	3.10
	PVA-PVDF	44.03	22.49	26.18	7.30	-
Inner	PVDF	53.60	5.92	39.44	1.04	-
surfaces	PVA-PSF	74.60	24.03	-	0.17	1.20
	PSF	82.59	14.01	-	0.18	3.22

Table III.3 XPS analyses of hollow fiber membranes

The PWP of the support hollow fiber membranes appears in Figure III.6. The PWP was equal for both dry and wet PVA-PVDF membranes at around 1,050 LMH/bar. However, while the PWP of a wet PVDF membrane was also about 1,050 LMH/bar, the PWP of a dry PVDF membrane showed no water flux. The PWPs of both dry and wet PVA-PSf membranes, as well as for a wet PSf membrane, were also similar (1,300 LMH/bar). Contrary to this, water would not permeate a dry PSf membrane. The presence or absence of a PVA coating led to a clear difference in the PWP of dry membranes. PVDF and PSf are hydrophobic (Figure III.4), which made it difficult for water to pass through the micropores of a dry support hollow fiber membrane. Hydrophilization with PVA allowed water to flow easily through these pores. The PVA-PSf membrane had a higher PWP than that of the PVA-PVDF membrane, because the PVA-PSf membrane had a larger average pore size and porosity, as shown in Table III.2.

Figure III.7 shows three microscope images of dried PVA-PVDF, PVDF, and insufficiently

PVA-coated PVDF hollow fiber membranes just after being immersed in water. An insufficiently PVA-coated membrane was fabricated by using a bore fluid with a lower PVA concentration (PVA:DMF:DI water = 1:85.5:13.5). The PVDF was discolored by the NaOH during the extraction and removal of silica, which gave it a brown color because of the double bond that was produced by the defluorination reaction of PVDF with NaOH. We found that when viewed in a dried state under a microscope, the color of the hollow fiber membranes following immersion in water appeared brown in the hydrophilic areas, but appeared white in the hydrophobic areas due to low compatibility with water. As shown in Figure III.7, incomplete hydrophilization caused only the portion without PVA to appear white. The PWP ratio for dry/wet membranes was reduced by the existence of portions that were not hydrophilized, as shown in Figure III.7. In the present study, the PWP ratio of the PVA-PVDF membrane and the microscope image of a cross-section revealed that all portions of this hollow fiber membrane had been hydrophilized by PVA.



Figure III.6 PWP of PVA-PVDF, PVDF, PVA-PSf, and PSf membranes

	PVA-PVDF	PVDF	Insufficient PVA coated PVDF*
Microscope images		0	No PVA
PWP ratio of	1000/	00/	(00)
dry membrane	100%	0%	60%
to wet membrane			

\* Bore fluid of PVA, DMF and DI water mixture (a weight ratio of 1:85.5:13.5) was used for membrane fabrication.

Figure III.7 Microscope images of dried membranes after immersion in water

# III.3.2. Characterization of interfacial polymerized PA hollow fiber membranes

PA active layers were formed on four types (PVA-PVDF, PVDF, PVA-PSf, and PSf) of membranes by interfacial polymerization. The interfacial polymerization conditions were the same for all four membranes. The interfacial polymerized membranes are referred to here as PA-PVA-PVDF, PA-PVDF, PA-PVA-PSf and PA-PSf.



Figure III.8 SEM images of interfacial polymerized membranes: (a) PVA-PVDF, (b) PA-PVA-PVDF, (c) PA-PVDF, (d) PVA-PSf, (e)PA-PVA-PSf, and (f) PA-PSf.

SEM images of the PA active layer of the interfacial polymerized hollow fiber membranes are shown in Figure III.8. Contrary to the smooth surfaces of PVA-PVDF (Fig. III.8 (a)) and PVA-PSf (Fig. III.8 (d)), the presence of a PA active layer on the support membrane was observed in PA-PVA-PVDF (Fig. III.8 (b)), PA-PVDF (Fig. III.8 (c)), PA-PVA-PSf (Fig. III.8 (e)), and PA-PSf (Fig. III.8 (f)) membranes. Careful observation near the top surface indicates the PA active layer on PA-PVA-PSf and PA-PSf penetrated the inner portion of the membrane cross sections. This was likely due to the larger pore sizes of the outer surface and to a broader distribution of the pore sizes in PVA-PSf and PSf (Fig. III.3) compared with PVA-PVDF and PVDF, which allowed the polymerization reaction to progress inside the membrane.

The IR data of two hollow fiber membranes after interfacial polymerization are shown in Figure III.9. Based on the IR data, the C=O bond stretching at around 1660 cm,<sup>-1</sup> the aromatic ring at 1,610 cm,<sup>-1</sup> and the C-N bond stretching at 1,547 cm,<sup>-1</sup> were all assigned to the PA active layer [33]. Similar data were also obtained for PA-PVDF and PA-PSf membranes, although the data are not shown.

Figure III.10 shows the breaking strength before and after interfacial polymerization. PVA-PVDF and PVDF membranes had a level of breaking strength that exceeded that of either PVA-PSf or PSf membranes. This is because the PVA-PVDF and PVDF membrane fabrication used solutions doped with a higher polymer concentration for the TIPS process. The breaking strength was the same before and after the interfacial polymerization.



Figure III.9 ATR-FTIR spectra of (a) PVA-PVDF and PA-PVA-PVDF, (b) PVA-PSf and

PA-PVA-PSf



Figure III.10 Breaking strengths of PVDF and PSf membranes before and after PA interfacial polymerization

# III.3.3. RO and FO performance of a TFC membrane

The performances in RO and FO testing (both AL-FS and AL-DS) of the four interfacial

polymerized hollow fiber membranes are summarized in Table III.4.

In the RO test, four membranes showed a similar *A* value of 2.2 LMH/bar. PA-PVA-PVDF and PA-PVA-PSf membranes showed higher Rs than PA-PVDF and PA-PSf membranes. The reason for the excellent rejection by the PVA-coated membranes was that during interfacial polymerization of the PA active layer, the PVA-coated membranes showed a high affinity for the aqueous MPD solution, and, therefore, it was easy for the MPD solution to penetrate the membrane, leading to the formation of a better PA layer. The PA-PSf membrane showed rejection that was quite low at 57.8%. Because PSf membranes have the large average size of the pores in the hydrophobic outer surface, the PA active layer of the PSf membrane was thicker (Figure III.11). Thus, while the PA-PSf membrane showed a lower level of rejection, it also showed a lower *A* value. Therefore, no FO testing was conducted for this membrane. On the PSf surface, the PA active layer was not very well formed, which may have been due to a pore size that was too large in this membrane. The PA-PVA-PSf membrane, however, showed a high level of rejection properties. Thus, the PVA coating played an important role in the interfacial polymerization of the PA active layer.

As for FO performance, a comparison of PA-PVA-PVDF and PA-PVDF membranes showed the same water flux values for both AL-FS and AL-DS modes, which indicated similar S values. This was because the PVA-PVDF and PVDF membrane support layers of PA-PVA-PVDF and PA-PVDF membranes, respectively, had the same pore structure except for the quality of hydrophilicity. This suggested that the presence of hydrophilicity in the support membrane did not have a large influence on water flux during FO testing. In addition, the PA-PVA-PVDF and PA-PVDF membranes had similar values for reverse-salt flux in AL-FS mode, but in AL-DS mode, the PA-PVDF membrane showed a higher level of reverse-salt flux. One reason for this higher reverse-salt flux was the lower rejection (*R*s) by the PA active layer of PA-PVDF. The PA-PVDF membrane. The reverse-salt flux in the AL-FS mode than of the PA-PVA-PVDF membrane. The reverse-salt flux

was sufficiently low in AL-FS mode, however, and no significant difference was observed. Higher values for water flux were obtained with PA-PVA-PSf membranes than for PA-PVA-PVDF membranes in both AL-FS and AL-DS modes. The reverse-salt flux was higher for PA-PVA-PSf membranes than for PA-PVA-PVDF membranes in both AL-FS and AL-DS modes. The PVA-PSf membrane showed a higher level of porosity compared with that of the PVA-PVDF membrane, as shown in Table III.2. Therefore, the ICP was suppressed for the PVA-PSf membrane, which led to a higher level of water flux. When the ICP was reduced, the PA-PVA-PSf membrane showed an *S* value that was lower than that of the PA-PVA-PVDF membrane. There are two reasons for the higher reverse salt flux of the PA-PVA-PSf membrane. One reason is the reduction in the ICP effect, which preserved a high salt concentration at the interface with the PVA-PSf layer and caused a high salt concentration difference across the PA active layer. Another reason can be attributed to the lower 1,000 ppm NaCl rejection (*R*s) by the active layer of the PA-PVA-PSf membrane.



Figure III.11 SEM analysis of PA active layer thickness of PA-PVA-PSf and PA-PSf.

	RO-test	RO-test		FO-test (AL-FS)		FO-test (AL-DS)	
FO membranes	A -value	<i>R</i> s	$J_{\mathrm{w}~(\mathrm{AL-FS})}^{\mathrm{FO}}$	$J_{\mathrm{S}~(\mathrm{AL-FS})}^{\mathrm{FO}}$	$J_{\mathrm{w}~(\mathrm{AL-DS})}^{\mathrm{FO}}$	$J_{\mathrm{S}(\mathrm{AL-DS})}^{\mathrm{FO}}$	[µm]
	[LMH/bar]	[%]	[LMH]	[gMH]	[LMH]	[gMH]	
PA-PVA-PVDF	2.26	93.4	10	2.6	13.5	16.9	1403
PA-PVDF	2.2	80.8	10.6	2.5	12.2	39.2	1252
PA-PVA-PSf	2.26	90.4	12.7	21.8	20.4	39.5	989
PA-PSf	2.23	57.8	n.d.	n.d.	n.d.	n.d.	n.d.

Table III.4 Performances of fabricated hollow fiber membranes in RO and FO tests

\*S-value was calculated from equation (4)

Figure III.12 shows the results of the water and reverse-salt fluxes in AL-FS mode for wet and dry PA-PVA-PVDF and PA-PVDF membranes at room temperature. Both the water and reverse-salt fluxes were greatly decreased for the dry PA-PVDF membrane, while those for the dry PA-PVA-PVDF membrane were similar. As described above, the PWP of the dry support PA-PVDF membrane was 0 LMH. Therefore, it was difficult for the draw solution to reach the PA active layer, which resulted in decreases in both the water and reverse-salt flux. Since the PWP of the dry PVA-PVDF membrane was equal to that of the wet membrane, even in the dry state, both the water and reverse-salt fluxes were similar to those obtained in the wet state. The above results confirmed that the PVA surface modification on the support membrane provided excellent FO performance for the TFC membrane. If sufficient performance can be achieved in a dry state, a reduction in transportation costs would be expected.



Figure III.12 Water and reverse-salt fluxes for PA-PVA-PVDF and PA-PVDF membranes under both wet and dry states in the AL-FS mode

# III.3.4 Comparison of RO and FO performances obtained in this work with those reported in the literature

The RO and FO performances obtained in this work were compared with those of the TFC membranes reported in the literature, as shown in Table III.5. During RO performance, TFC membranes fabricated in this study had a higher *A*-value and a lower *B*-value compared with those reported in the literature. During FO performance, these membranes had sufficient water and reverse-salt fluxes based on comparison with the performance data in the literature. On the other hand, the *S*-value was quite large compared with reports in the literature, because these membranes were thicker (200 µm) and the ICP was not sufficiently suppressed. This study was performed for the development of mass production technologies such as a roll-to-roll processing, and, therefore, it was focused on physical strength rather than on either FO performance or *S*-values. Although the *S*-value was not sufficiently low, both the FO performance and the *S*-value could be improved in the future either by reducing the membrane support thickness or by using a support with higher porosity.

In particular, the PA-PVA-PVDF and PA-PVDF membranes maintained excellent physical

strength. Their breaking points occurred at more than 10 MPa with collapse pressures of 1.6 MPa from the outside and 2.0 MPa from the inside, which indicated an extremely high level of physical durability due to the use of the TIPS process.

#### **III.4.** Conclusions

We developed a new hydrophilization method that can be used to prepare hydrophilic hollow fiber membranes via the diffusion of PVA from the bore fluid to the outer membrane surface in the membrane fabrication process. This hydrophilization method allowed us to coat the entire surface of a hollow fiber membrane with PVA. By this hydrophilization method, hydrophilic PVDF and PSf hollow fiber membranes could be fabricated via TIPS and NIPS, respectively.

Interfacial polymerization was carried out on both PVDF and PSf support membranes in the preparation of TFC membranes; and the RO and FO performances of these membranes were evaluated. The 1,000 ppm NaCl rejection by the TFC membrane with a hydrophilized support membrane during RO testing was higher than that with a non-hydrophilized support membrane. Measurements of FO performance using wet TFC membranes showed no differences when using either hydrophilized or non-hydrophilized support membranes. However, the dry TFC membranes with non-hydrophilized support showed a much lower FO performance. We found that hydrophilization via the PVA diffusion method resulted in FO performance by the dry membranes that was similar to that of the wet membranes. The TFC membrane with PVDF via TIPS processing had excellent physical strength. The information discussed here should be useful for developing mass production technologies and high-performance TFC PVDF membranes.

Mamhuana		Thislmoss	Breaking	RO test		FO test (AL-FS) <sup>*1</sup>			
name	Materials	I mckness	strength	A -value	B-value	$J_{ m w}$	$J_{s}$	S-value	References
name		լրույ	[MPa]	[LMH/bar	[LMH]	[LMH] [gMH] [µm]			
PA-PVA-PVDF	PVDF	201	10.5	2.26	0.16	10.0	2.58	1403	This work
PA-PVDF	PVDF	201	10.8	2.20	0.52	10.6	2.45	1252	This work
PA-PVA-PSf	PSf	198	6.2	2.26	0.24	12.7	21.75	989	This work
PAN-0	PAN	100	4.1	2.01	0.68	16.6	6.5	549	[13]
PAN-30	PAN	100	4.1	1.98	0.70	17.0	6.0	499	[13]
PAN-60	PAN	50	8.0	2.20	1.52	24.6	19.2	305	[13]
TFC-FO with	DEC	110	5.9	1.18	0.14	32.1 <sup>*2</sup>	6.2 <sup>*2</sup>	219 <sup>*2</sup>	[34]
PES <sub>water</sub> supports	PES								
TFC-FO with	DEC	110	7.0	1.64	0.00	24.1*2	<b>7</b> 1*2	aca*2	[24]
PESwater/NMP supports	PES	110	/.0	1.64	0.28	34.1 -	7.1 -	252 -	[34]
TFC-FO with	DEC	110	5.0	1.02	0.25	• • •*2	o o*2	*2	[2,4]
PES <sub>water/NMP/PEG</sub> supports	PES	110	5.8	1.83	0.35	34.5 -	9.9 -	261 -	[34]
TFC-TB1	Matrimid®	215	5.1	0.97	0.11	6.3	1.0	1670	[35]
TFC-TB2	Matrimid®	197	4.9	1.42	0.18	9.3	2.0	110	[35]
TFC-TB3	Matrimid®	203	5.5	1.51	0.44	9.4	2.1	1100	[35]
HF-C	CTA	36	n.d.	0.55	0.04	8.0	0.59	639	[36]

Table III.5 Compares breaking strength, RO performance and FO performance in TFC PA hollow fiber membranes with that reported in the literature.

\*1 1.0 M NaCl was used as draw solution, \*2 2.0 M NaCl was used as a draw solution.

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# Chapter IV Preparation of high performance FO membrane using a highly porous PVDF hollow fiber membrane support

# **IV.1. Introduction**

In Chapter III, we succeeded to fabricate a FO membrane with PVDF hollow fiber membrane support, however the FO performance was not sufficient. Therefore, we conducted research on FO membranes with more porous PVDF hollow fiber membrane support that can suppress ICP, and we challenged to obtain high FO performance compared with literatures.

The forward osmosis (FO) method is attracting attention as a new desalination technique to replace the reverse osmosis method [1, 2]. Thin-film composite (TFC) membranes composed of an aromatic polyamide (PA) active layer and a porous support layer can be prepared via interfacial polymerization and used as FO membranes. In the FO process, the osmotic pressure difference between the feed solution (FS) and draw solution (DS) provides the driving force to move water from the FS side to the DS side. It is necessary to suppress internal concentration polarization (ICP) in the support layer to maintain a high osmotic pressure difference [3, 4]. The support membrane must therefore be thin and have a highly porous structure of low tortuosity.

Poly(vinylidene difluoride) (PVDF) is used as the core material of hollow fiber membranes such as microfiltration (MF) and ultrafiltration (UF) membranes because of its high physical and chemical stabilities [5]. PVDF is therefore one of the most promising support membranes for FO membrane processes. Non-solvent-induced phase separation (NIPS) [6], thermally induced phase separation (TIPS) [7], and phase separation methods that combine these two methods have been studied as mainstream techniques for fabricating PVDF hollow fiber membranes. PVDF hollow fiber membranes with interconnected bicontinuous structures, closed-cell structures, finger-like

macrovoid structures, and spherulite structures have been produced. MF and UF membranes with an interconnected bicontinuous structure are preferable because of their excellent pure water permeances (PWPs) and mechanical strengths. PVDF membranes with a well-developed interconnected bicontinuous structure with high porosity, low tortuosity, and/or a thick stem have low resistance to water permeation, which leads to a high PWP and high strength. However, it is difficult to control the interconnected bicontinuous structure because of the difficulty of controlling the phase separation method (TIPS, NIPS, and TIPS–NIPS combination) for PVDF production [8].

In the TIPS method, the pore structure can be determined primarily based on the affinity between PVDF and a poor solvent. Gu et al. reported that when solvents such as dibutyl phthalate (DBP), dimethyl phthalate, dioctyl sebacate, and dioctyl adipate were used as the poor solvent, formation of the spherulite structure based on solid–liquid (S–L) phase separation was preceded by PVDF crystallization [9]. Su et al. reported that the compatibility of the solvent and PVDF decreased, and the crystallization temperature increased, in the order  $\gamma$ -butyrolactone (GBL), propylene carbonate, DBP, and dibutyl sebacate [10]. Yang et al. reported that when diphenyl ketone was used as the poor solvent, an interconnected bicontinuous structure was formed based on liquid–liquid (L–L) phase separation [11]. Matsuyama et al. reported that the interconnected bicontinuous structure and spherulite structure can be controlled by using glycerol triacetate (triacetin) and glycerol, and changing the solvent affinity [12]. An interconnected bicontinuous structure can be formed easily via the TIPS method, but it is still difficult to control the interconnected bicontinuous structure precisely because the TIPS method uses heat as the driving force for phase separation.

In the NIPS method, the pore structure can be determined primarily based on the affinity between the PVDF stock solution and the non-solvent in the outer coagulation solution. For example, the effects of the affinity in the outer coagulation solution on the structural behavior have been studied. It has been reported that in the PVDF/dimethylformamide system, the use of a low-affinity non-solvent (water) leads to formation of a finger-like macrovoid structure because of rapid uptake of the non-solvent [13]. However, addition of a high-affinity non-solvent (1-octanol) decreases the speed of solvent uptake, which leads to formation of a spherulite structure based on S–L phase separation, preceded by PVDF crystallization [14]. It has also been reported that addition of ethanol to the outer coagulation solution and bore fluid to change the coagulation speed led to formation of hollow fiber membranes with both an interconnected bicontinuous PVDF membrane structure and a finger-like macrovoid structure [15, 16]. Although it is possible to fabricate a structure with a thicker stem via the NIPS method by controlling the coagulation speed, it is difficult to suppress formation of a macrovoid structure and a crystal structure with PVDF, which is a crystalline polymer. In some studies, poly(vinylpyrrolidone) (PVP) has been used as an additive to suppress PVDF crystallization and promote L–L phase separation. However, PVDF membranes containing PVP have the problem of formation of macrovoid structures because of the improved affinity with the outer coagulation solution as a result of the high hydrophilicity of PVP [17, 18].

There have also been several reports of phase separation methods that combine NIPS and TIPS [19-21]. For example, Qin et al. reported a modified TIPS method that used dimethylacetamide for NIPS (a good solvent for PVDF) and GBL for TIPS (a poor solvent for PVDF) [22]. Hassankiadeh et al. reported an improved TIPS method, in which PolarClean (a poor solvent for PVDF), which has excellent water solubility, was used [23]. Lee et al. reported a dual-layer hollow fiber membrane that consisted of a coating layer, which was fabricated via the NIPS method, on a support layer made by using the TIPS method [24]. However, the bicontinuous structures reported to date have been interconnected but too dense, or consisted of a combination of macrovoid and spherulite structures. This leads to lower mechanical strengths and water permeances.

As mentioned above, various methods for the fabrication of PVDF membranes by using phase separation methods such as NIPS, TIPS, and combinations of NIPS and TIPS have been studied.

However, a method for fabrication of PVDF membranes with a well-developed interconnected bicontinuous structure has not yet been reported.

Our objective was to develop a novel PVDF hollow fiber membrane with a well-developed interconnected bicontinuous structure for use in FO membranes. We have employed a poor solvent for TIPS as a solvent, and investigated use of the PVDF/PVP/GBL system in high-temperature rapid non-solvent-induced phase separation (HTR-NIPS). We aimed to fabricate an interconnected bicontinuous structure with a thick stem by using PVP as an additive to suppress crystallization and gelation of PVDF. Furthermore, we aimed to promote faster phase separation of PVDF and fabrication of a thicker stem in the interconnected bicontinuous structure by using GBL, which is a poor solvent for PVDF and primarily used for TIPS. We determined the upper critical solution temperature (UCST) and gelation temperature of the PVDF/GBL/PVP system. We performed membrane fabrication at an outer coagulation solution temperature that was higher than the UCST and gelation temperature, and investigated the effects of the HTR-NIPS method, in which NIPS was promoted by using the poor solvent GBL, on the interconnected bicontinuous structure. We also fabricated FO membranes using PVDF as a support membrane with a well-developed interconnected bicontinuous structure, and investigated the effects of the support layer structure on the FO performance.

# **IV.2.** Experimental

# IV.2.1. Materials

Poly(vinylidene difluoride) was Kynar 741 purchased from Arkema S.A., Paris, France. Poly(vinylpyrrolidone) was Sokalan K-90P purchased from BASF Co., Ludwigshafen, Germany. Poly(ethylene glycol) was PEG 600 purchased from Fujifilm Wako Pure Chemical Co., Osaka, Japan. GBL (purity >99.0%), glycerin (purity >99.5%), hydrogen peroxide (30.0%–35.5% aqueous solution), copper(II) chloride (purity >95.0%), and sodium sulfate (purity >99.0%) were purchased from the Fujifilm Wako Pure Chemical Co. (Osaka, Japan).

The reagents used for interfacial polymerization were m-phenylenediamine (MPD, purity >95.0%), 1,3,5-benzentricarbonyl trichloride (TMC, purity >98.0%), isophthaloyl dichloride (IPC, purity >99.0%), (±)-10-camphorsulfonic acid (CSA, purity>98.0%), sodium dodecyl sulfate (SDS, purity >95.0%), triethylamine (TEA, purity >99.0%), hexamethylphosphoric triamide (HMPA, purity >97.0%), and n-hexane (purity >99.0%). These reagents were purchased from the Fujifilm Wako Pure Chemical Co. (Osaka, Japan).

## **IV.2.2.** Fabrication of PVDF hollow fiber membranes

PVDF hollow fiber membranes were fabricated via HTR-NIPS. For preparation of the stock solution, PVDF, GBL, and PVP (weight ratios 25:63:12) were mixed and heated at 120 °C through a twin-screw extruder. For preparation of the bore fluid, GBL and Gly (15:85 as weight ratio) were mixed. These solution and fluid were extruded into a spinneret for fabrication of the membrane. Extrusion of these solution and fluid into a temperature-controlled outer coagulation solution with 10 wt% of a sodium sulfate aqueous solution (to keep high outer surface pore occupancy with salting-out effect; Figure IV.1) at the rate of 7.5 m/min through an air gap at a distance of 4 cm, enabled fabrication of PVDF hollow fiber membranes with various outer and internal diameters. The

obtained PVDF hollow fiber membranes were immersed in a hot-water bath (90 °C) for 1 h to remove GBL and some of the PVP. The PVDF hollow fiber membranes were then immersed in an aqueous solution containing hydrogen peroxide (1%) and copper(II) chloride (1 ppm) for 2 h to cross-link the PVP. As a result, PVPs are cross-linked each other and molecular weight has increase, therefore PVP was insoluble in water (PVDF and PVP do not have cross-link). A PVDF hollow fiber membrane was prepared by the same process but with PEG as the additive instead of PVP for comparison.

Five types of PVDF hollow fiber membranes with different diameters and thicknesses were fabricated. The external and internal diameters of the hollow fiber membrane were adjusted to 800/600  $\mu$ m (PVDF-A), 1000/600  $\mu$ m (PVDF-B), and 1250/750  $\mu$ m (PVDF-C, PVDF-D, and PVDF-E). The temperatures of the outer coagulation solution were controlled at 70 °C for PVDF-A, PVDF-B, and PVDF-D, 60 °C for PVDF-C, and 80 °C for PVDF-E.



Figure IV.1 Effect of outer coagulation solution (DI water vs 10% sodium sulfate aqueous solution)

# **IV.2.3.** Preparation of PA-PVDF membranes

A PA active layer was prepared on the outer surfaces of the PVDF membranes via interfacial polymerization. The preparation conditions were summarized in supplementary data; Table IV.1. The bore side of hollow fiber membranes was blocked. The hollow fiber membranes were slowly immersed in a MPD aqueous solution for 2 min. Excess MPD solution was removed and then the hollow fiber membranes were slowly immersed in an *n*-hexane solution containing TMC and IPC for 1 min. A PA active layer was polymerized on the outer surfaces of the membranes. The hollow fiber membranes were heated and dried for 4 min at 120 °C. After that the membranes were washed with pure water to yield TFC membranes [25-27].

Table IV.1 Conditions for preparation of PA active layers via interfacial polymerization on PVDF hollow fiber membranes

MPD aqueous solution					TMC-hexane solution			Drying		
MPD	TEA	CSA	SDS	HMPA	Immersion time	TMC	IPC	Immersion time	temp.	time
		(wt%)			(min)	(wt%)	(wt%)	(min)	(°C)	(min)
2	1.1	2.3	0.15	1.0	4	0.12	0.03	2	120	4

# **IV.2.4.** Characterization of membranes

The surface and cross-sectional structures of the membranes were examined by scanning electron microscopy (SEM; Hitachi S-300N, Hitachi Co., Tokyo, Japan). The external and internal diameters of the PVDF membranes were measured by using a microscope (VHX-5000 digital microscope, Keyence Co., Tokyo, Japan). The PWPs of the PVDF membranes were determined by preparing a membrane module (effective length of 10 cm) by blockling one end of the hollow fiber membrane.

The PWPs (L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>) were estimated from the weight of water permeated in 1 min under condition with 0.5 bar. The PWPs of hollow fiber membrane modules in the dry and wet states were determined. The PWP in the wet state was determined by immersing for 10 min in 50wt% ethanol, washing for 10 min with pure water, after that measuring the PWP.

The pore size and surface pore occupancy of the PVDF hollow fiber membranes were determined from SEM images of the outer surface of the PVDF hollow fiber membranes. The SEM images were analyzed to obtain the pore area with Image-Pro Plus (Planetron Co., Tokyo, Japan), which was then used to determine the pore size distribution and surface pore occupancy. The total porosity (%) of the PVDF hollow fiber membranes was determined from the difference between the weights of the hollow fiber membranes in the dry and wet states.

$$porosity(\%) = \frac{(wet state weight(g)) - (dry state weight(g))}{wet state weight(g)} \times 100$$
(IV.1)

Attenuated total reflectance Fourier-transfer infrared (ATR-FTIR) spectra of the PVDF hollow fiber membranes were obtained with an IR spectrophotometer (JIR-5500, JEOL Co., Tokyo, Japan). The mechanical strengths of the PVDF hollow fiber membranes were investigated by conducting tensile tests. Hollow fiber membranes of length 5 cm were stretched (at a rate of 100 mm/min) in water at 25 °C by using an autograph (AG-Xplus, Shimadzu Co., Kyoto, Japan). The gelation temperature and UCST were estimated as follows. A stock solution was dissolved at 110 °C. The solution viscosity was determined by using a rotary rheometer (ARES-G2, TA Instruments Japan Inc., Tokyo, Japan) at a cooling speed of 3 °C/min, strain of 3%, and angular speed of 10 rad/s in the temperature range –20 to 80 °C. Solution viscosity–temperature curves were constructed and used to estimate the gelation temperature. The UCST was determined from the cloud points of the stock solution at various temperatures.

# IV.2.5. FO test conditions for PA-PVDF hollow fiber membranes

An experimental apparatus and test module to investigate the FO performances of the TFC membranes were prepared with the same method with reference [27]. In the FO tests, PWP were measured with the active layer facing the feed solution (AL-FS) with the same condition with reference [27]. For the DS side, sodium chloride solutions at concentrations between 0.5 and 2.0 M were used as a DS. The water flux ( $J_w$ ; L m<sup>-2</sup> h<sup>-1</sup>) and the reverse-salt flux ( $J_s$ ; g m<sup>-2</sup> h<sup>-1</sup>) were estimated from the changes in the weight and electrical conductivity of the FS. Excel data provided by Tiraferri et al. and the  $J_w$  and  $J_s$  values obtained from the FO tests were used to calculate the water permeability coefficient A (L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>), salt reverse diffusion coefficient B (L m<sup>-2</sup> h<sup>-1</sup>), and the structural parameter S, by using equations (IV.2) and (IV.3).

$$J_{\rm w} = A \left( \frac{\pi_{\rm DS} \exp\left(-\frac{J_{\rm w}S}{D}\right) - \pi_{\rm FS} \exp\left(\frac{J_{\rm w}}{k}\right)}{1 + \frac{B}{J_{\rm w}} (\exp\left(\frac{J_{\rm w}}{k}\right) - \exp\left(-\frac{J_{\rm w}S}{D}\right))} \right) \quad ({\rm IV.2})$$
$$J_{\rm S} = B \left( \frac{C_{\rm DS} \exp\left(-\frac{J_{\rm w}S}{D}\right) - C_{\rm FS} \exp\left(\frac{J_{\rm w}}{k}\right)}{1 + \frac{B}{J_{\rm w}} (\exp\left(\frac{J_{\rm w}}{k}\right) - \exp\left(-\frac{J_{\rm w}S}{D}\right))} \right) \quad ({\rm IV.3})$$

$$S = \frac{\tau t}{\varepsilon}$$
 (IV.4)

 $\pi_{\rm DS}$  and  $\pi_{\rm FS}$  are the osmotic pressures of DS and FS,  $C_{\rm DS}$  and  $C_{\rm FS}$  are the DS and FS concentrations, k is the feed solute mass transfer coefficient, and D is the bulk diffusion coefficient of the draw salt. The structural parameter S (µm) is expressed as the product of the membrane thickness t (µm) and tortuosity  $\tau$  (–), divided by the porosity  $\varepsilon$  (–), as shown in equation (IV.4) [28, 29].

#### **IV.3. Results and discussion**

## IV.3.1. Formation of interconnected bicontinuous structure on PVDF hollow fiber membranes

It has been reported that thermoreversible gelation and crystallization occur in a GBL solution because PVDF is a crystalline polymer [30]. During the phase separation process, in which the stem becomes thick, phase separation terminates when gelation occurs because the viscosity of the solution suddenly increases. This results in formation of a macrovoid structure. It is believed that when crystallization occurs the system forms a spherulite structure. To develop an interconnected bicontinuous structure, it is necessary to perform phase separation under conditions where gelation and subsequent crystallization do not occur during L–L phase separation to gain a thicker stem. It has been reported that addition of PVP suppresses crystallization of PVDF [31, 32]. We therefore also studied the effects of addition of PVP to a solution of PVDF in GBL on gelation and the phase separation behavior.

Figure IV.2(a) shows the gelation temperatures in three-component systems, i.e., PVDF/GBL/PVP and PVDF/GBL/PEG (PEG is a commonly used additive for phase separation), and in the two-component system PVDF/GBL. As shown in Figure IV.2(a), in the system without PVP, the viscosity of the stock solution increased rapidly with decreasing stock solution temperature, which advanced gelation. In contrast, the viscosity of the PVDF/GBL/PVP system did not increase rapidly, although the viscosity was high. These results clearly suggest that addition of PVP can suppress gelation and subsequent crystallization of PVDF. Figure IV.2(b) shows the phase separation temperatures. In the three-component system PVDF/GBL/PVP, the stock solution, which was transparent at 60 °C, became cloudy near 50 °C. The phase separation temperature for the stock solution in a three-component system consisting of PVDF/GBL/PVP was therefore between 50 and 60 °C. Similarly, the phase separation temperature for the three-component system PVDF/GBL/PEG was observed to be between 70 and 80 °C. To obtain a PVDF membrane with a well-developed interconnected bicontinuous structure, fabrication needs to be performed at a temperature higher than the UCST to prevent at least TIPS-derived phase separation to gain a thicker stem. In the phase separation process the polymer concentration of dope solution may increase with the transportation of solvent from dope solution to coagulation bath, therefore we also performed another test in different dope concentration (PVDF/GBL/PVP=27/61/12). However, we confirmed that the gelation temperature was not observed significantly, and phase separation temperature was not changed significantly (Figure IV.3).



Figure IV.2 (a) Changes in viscosity of different systems at various temperatures and (b) photographs of different systems at various temperatures.



Figure IV.3 Gelation temperature and phase separation temperature in the PVDF/GBL/PVP = 27/61/12 system.

Composition	Coagulation						
of dope	bath	Cross section SEM images					
	temperature			(0)*0*			
	20 °C		<u>бо µm</u>				
PVDF/GBL/PVP =25/63/12	60 °C	200 µm					
	80 °C		50 µm	See a			
	20 °C	200 µm	so μm				
PVDF/GBL/PEG =25/63/12	60 °C	200 µm	стания 50 µm				
	80 °C	200 μm	ССС 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1				

Figure IV.4 Cross-sectional SEM images of PVDF/GBL/PVP and PVDF/GBL/PEG systems

For the three-component systems PVDF/GBL/PVP and PVDF/GBL/PEG, we performed SEM observations of the hollow fiber membrane at various outer coagulation solution temperatures (Figure IV.4). In the case of the PVDF/GBL/PEG system, a spherulite hollow fiber membrane was formed with advanced crystallization, regardless of whether the outer coagulation solution temperature was 20, 60, or 80 °C. When the outer coagulation solution temperature was 20 or 60 °C, which was lower than the UCST, and hence, the structure was assumed to have a spherulite character derived from TIPS. In contrast, when the outer coagulation solution temperature was 80 °C, which was higher than the UCST, but the structure was spherulite. The three-component system PVDF/GBL/PEG leads to gelation and subsequent crystallization, therefore we believe that gelation and crystallization occurred during NIPS-derived phase separation. The gelation and crystallization then stopped spinodal phase separation, which forms the interconnected bicontinuous structure. This phase separation behavior of the PVDF/GBL/PEG system therefore results in formation of macrovoid and spherulite structures.

In the case of the PVDF/GBL/PVP system, when the hollow fiber membrane was sampled at an outer coagulation solution temperature of 20 °C, the hollow fiber membrane had a spherulite structure with advanced crystallization as a result of TIPS, because the outer coagulation solution temperature was lower than the UCST. In contrast, when the hollow fiber membrane was sampled at an outer coagulation solution temperature of 60 or 80 °C, no progression of TIPS was observed. The addition of PVP suppressed gelation. This confirms the formation of a well-developed interconnected bicontinuous structure for the PVDF/GBL/PVP system prepared at 60 or 80 °C with PVP.

The above results suggest that fabrication of PVDF membranes with a well-developed interconnected bicontinuous structure requires the following fabrication conditions to be satisfied. (1) The stock solution composition must not have a gelation temperature. (2) The membrane must be

fabricated at an outer coagulation solution temperature higher than the UCST.

#### IV.3.2. Characterization of PVDF hollow fiber membranes

PVDF hollow fiber membranes (PVDF-A, PVDF-B, PVDF-C, PVDF-D, and PVDF-E) were prepared via the HTR-NIPS method in three-component systems consisting of PVDF/GBL/PVP under the fabrication conditions (1) and (2) described in section IV.3.1.

Figure IV.5 summarizes the SEM data for the PVDF hollow fiber membrane samples in this study. Table IV.1 summarizes the fabrication conditions, outer diameter, inner diameter, modal pore size on the outer surface, surface pore occupancy, and porosity of each hollow fiber membrane. For the samples PVDF-A, PVDF-B, and PVDF-D, only their outer and inner diameters changed at a constant outer coagulation solution temperature of 70 °C. For PVDF-A, the outer diameter was 833  $\mu$ m, the inner diameter was 644  $\mu$ m, and the thickness was 95  $\mu$ m. For PVDF-B, the outer diameter was 967  $\mu$ m, the inner diameter was 607  $\mu$ m, and the thickness was 180  $\mu$ m. For PVDF-D, the outer diameter was 1247  $\mu$ m, the inner diameter was 749  $\mu$ m, and the thickness was 249  $\mu$ m. An interconnected bicontinuous structure with a thicker stem was formed in the case of thicker membranes. This is presumably because at a greater thickness, liquid exchange at the center is more difficult, which enables fabrication of an interconnected bicontinuous structure with a thickness did not change the properties of the hollow fiber membrane, such as pore size distribution on the outer surface of the membrane, surface pore occupancy, and porosity (Table IV.2, Figure IV.6a).

The samples PVDF-C, PVDF-D, and PVDF-E were fabricated by changing only the outer coagulation solution temperature, and maintaining constant outer and inner diameters. We confirmed that PVDF-C, PVDF-D, and PVDF-E had similar outer diameters, inner diameters, and thicknesses. The stem thickness in the interconnected bicontinuous structure in the direction of the membrane cross-section increased with increasing outer coagulation solution temperature. Higher outer coagulation solution temperatures enabled membrane fabrication at temperatures higher than the

gelation temperature; S–L phase separation was therefore suppressed at high temperatures, even if a thicker stem was formed during phase separation, which led to growth of the interconnected bicontinuous structure. The pore size distribution on the outer surface of the membrane widened with increasing outer coagulation solution temperature. The mean pore size increased from 28 to 100 nm with increasing temperature from 60 to 80  $^{\circ}$  C. However, the surface pore occupancy and porosity did not change (Table IV.2, Figure IV.6b).



Figure IV.5 SEM images of fabricated PVDF hollow fiber membranes

All the hollow fiber membranes showed unique pore structures in which interconnected bicontinuous structures had been formed at the micrometer scale. In particular, PVDF-E had a much thicker stem in the interconnected bicontinuous structure.

PVDF membrane name	Outer coagulation solution temperature (°C)	Outer diameter (μm)	Inner diameter (μm)	Mode pore size on the outer surface (nm)	Surface pore occupancy on the outer surface (%)	Total porocity (%)
PVDF-A	70	$833\pm25$	$644\pm20$	63	$17 \pm 2$	$72 \pm 3$
PVDF-B	70	$967\pm19$	$607\pm18$	45	$17 \pm 2$	$73\pm3$
PVDF-C	60	$1264\pm24$	$730\pm15$	28	$16 \pm 2$	$74 \pm 3$
PVDF-D	70	$1247\pm22$	$749 \pm 17$	50	$16 \pm 2$	$72\pm3$
PVDF-E	80	$1270\pm24$	$755\pm18$	100	$18 \pm 2$	$72\pm3$

Table IV.2 Specifications of PVDF hollow fiber membranes



Figure IV.6 Pore size distributions of outer surfaces of PVDF hollow fiber membranes: effects of membrane thickness (a) and outer coagulation solution temperature (b).

Figure IV.7(a) shows the PWP measurement results for the hollow fiber membranes. Figure IV.7(b) shows the membrane breaking strengths. Figure IV.7(c) shows the relationships between the PWP and breaking strength compared with literature data for PVDF membranes [12, 19, 22-24, 33-35]. The PVDF hollow fiber membrane samples prepared in this study had excellent PWP values. This can be attributed to formation of well-developed interconnected bicontinuous structures because of their low resistance to the passage of pure water. The PWPs of the PVDF membranes in this study were equally high in the dry and wet states, therefore we can reasonably assume that the entire membrane surface was hydrophilized by cross-linking and insolubilization of PVP. The effect of the outer coagulation solution temperature on the PWP was therefore greater (PVDF-C vs PVDF-D vs PVDE-E) than the effect of the thickness of the hollow fiber membrane (PVDF-A vs PVDF-B vs

PVDF-D). A comparison of the membrane strengths showed that, as was the case for the PWP, the strength depended more on the temperature of the outer coagulation solution (PVDF-C vs PVDF-D vs PVDF-E) than on the thickness of the hollow fiber membrane (PVDF-A vs PVDF-B vs PVDF-D). These results suggest that a thicker stem in the interconnected bicontinuous structure is related to improvements in the PWP and strength. Compared with those reported in previous studies, our membranes had sufficient strength despite being more permeable, and it was also shown that our membranes located upper side of the upperbound between PWP and breaking strength proposed by Kim [36]. This is an excellent property of the interconnected bicontinuous structure fabricated in this study. Measurements of the burst pressure from the inner side of the hollow fiber showed that all the hollow fiber membranes had a burst pressure of 0.5 MPa or more.



Figure IV.7 (a) PWPs and (b) breaking strengths of PVDF hollow fiber membranes, (c) the relationships between PWP and breaking strength compared with literature data. The upperbound between PWP and breaking strength was calculated from the equation proposed by Kim [36]

# IV.3.3. Characterization of PA-PVDF hollow fiber membranes

A PA active layer was prepared on the PVDF support membranes (PVDF-A, PVDF-B, PVDF-C, PVDF-D, and PVDF-E) via interfacial polymerization (PA-PVDF-A, PA-PVDF-B, PA-PVDF-C, PA-PVDF-D, and PA-PVDF-E).



Figure IV.8 SEM images of outer surfaces and outer cross-sections of PVDF-A (before interfacial polymerization) and PA-PVDF-A (after interfacial polymerization)

Figure IV.8 shows SEM images of the outer surface and outer cross-section of PVDF-A (before interfacial polymerization) and PA-PVDF-A (after interfacial polymerization). The figure confirms formation of PA-PVDF-A, i.e., formation of a PA active layer on the outer surface of the support

layer via interfacial polymerization. Figure IV.9 shows FTIR spectra of the hollow fiber membranes before and after interfacial polymerization. The FTIR spectrum of PVDF-A shows a C=O stretching vibration peak from cross-linked PVP in PVDF-A. This indicates hydrophilization by PVP. The C=O stretching vibration of PVP is usually near 1680 cm<sup>-1</sup> but can shift to near 1700 cm<sup>-1</sup> as a result of a cross-linking reaction [37]. These data show that the PVDF membrane was covered by cross-linked PVP. The FTIR spectrum of PA-PVDF-A shows a high-intensity absorbance from the C=O stretching vibration, at 1660 cm<sup>-1</sup>, and peaks from the aromatic ring, at 1610 cm<sup>-1</sup>, and C–N stretching vibration, at 1547 cm<sup>-1</sup>. These results indicate successful formation of a PA active layer [38]. The other hollow fiber membranes prepared in this work provided similar data, which confirms that all the PVDF membranes were covered with PA.



Figure IV.9 ATR-FTIR spectra of PVDF-A and PA-PVDF-A

# IV.3.4. FO performances of PA-PVDF hollow fiber membranes

The water fluxes,  $J_w$ , of the PA-PVDF membranes were determined by performing FO tests; the  $J_w$  values as a function of the sodium chloride concentration of the DS are summarized in Figure IV.10. Figure IV.11 shows the relationship between the thickness of the PVDF hollow fiber

membrane support layer and  $J_w$ , and that between the modal pore size in the outer surface and  $J_w$ , when 1.0 M sodium chloride was used as the DS.

We investigated the effects of the thickness of the hollow fiber membrane substrate by comparing the results for PA-PVDF-A, PA-PVDF-B, and PA-PVDF-D. The comparison showed that  $J_w$ increased as the membrane became thinner, and PA-PVDF-A, with the thinnest membrane, had the highest  $J_w$  value. This is because as the membrane became thinner, the membrane thickness t in equation (IV.4) decreased and reduced the structural parameter S, which suppressed the ICP and led to a rise in  $J_w$ . The values for of PA-PVDF-C, PA-PVDF-D, and PA-PVDF-E were compared to clarify the effects of the modal pore size and cross-sectional pore size on the outer surface of the hollow fiber membrane substrate. The  $J_w$  value for PA-PVDF-E, which had the highest modal pore size and cross-sectional pore size, was slightly higher than those for the other two membranes. The PVDF-E support layer had the largest modal pore size and cross-sectional pore size on the outer surface and had the thickest stem in the interconnected bicontinuous structure, therefore the structural parameter S decreased, which can lead to suppression of the ICP and a rise in  $J_{\rm w}$  via the contribution of the low tortuosity  $\tau$  in equation (IV.4). The tortuosity  $\tau$  values estimated from the FO test results were about 2.2 for PA-PVDF-A and 1.0-1.2 for PA-PVDF-B, PA-PVDF PA-PVDF-C, PA-PVDF-D, and PA-PVDF-E (supporting information; Figure IV.12). Such low  $\tau$  values for all the membranes imply the formation of well-developed interconnected bicontinuous structures; these results are consistent with the SEM images (Figure IV.5). In addition, the relationship between the product of  $J_w$  and the thickness t, and the tortuosity  $\tau$  for the PA-PVDF membranes shows that the water transport (expressed by  $J_w \times t$ ) was clearly high when the tortuosity  $\tau$  was low (supporting information; Figure IV.13). These results suggest that the interconnected bicontinuous structure of the PVDF membranes is a key factor in achieving high water permeation of FO membranes. The support layers for all the PVDF membranes were prepared with the same stock solution composition

but under different membrane fabrication conditions, and their values for parameters such as porosity,  $\varepsilon$ , and surface pore occupancy on the outer surface were similar. These results show that the changes in the structural parameter S and changes in  $J_w$  are related to the support layer thickness t and  $\tau$ , owing to the changes in the modal pore size and cross-sectional pore size on the outer surface.

Notably, the differences among the *J*<sub>w</sub> values for PA-PVDF-C, PA-PVDF-D, and PA-PVDF-E were not as large as expected. Lee et al. recently reported the results related to the structure of a substrate suitable for suppressing the ICP in FO membranes. According to their study, the surface pore occupancy of the substrate is most effective for suppressing the ICP, and improvements in the cross-sectional shape of the substrate does not contribute to ICP suppression [39]. The results for PA-PVDF-C, PA-PVDF-D, and PA-PVDF-E are consistent with those reported by Lee et al. Despite the improvement in the cross-sectional shape of the substrate, the surface pore occupancy was almost the same. Improving the surface pore occupancy to achieve a better performances is a challenge.



Figure IV.10 Comparison of  $J_w$  values obtained from FO tests (AL-FS mode) for PA-PVDF hollow fiber membranes



Figure IV.11 Effects of thickness of support membrane and modal pore size in outer surface of support membrane on  $J_w$ 



Figure IV.12 Relationship between  $J_w$  and tortuosity  $\tau$  values of support membranes



Figure IV.13 Relationship between ( $J_{
m w}$  × thickness t) and tortuosity  $\tau$  of support membranes

Table IV.3 summarizes the FO performances of the PA-PVDF hollow fiber membranes in this study and compares them with those of PA hollow fiber membranes reported in the literature [2, 27, 40-46]. The *S* values of the PA-PVDF hollow fiber membranes fabricated in this study were lower than those for previously reported PA hollow fiber membranes. Although FO flat sheet membranes with significant low S values have recently emerged [46], the thinnest membrane, i.e., PA-PVDF-A, had a particularly low *S* value in hollow fiber type, and therefore provided a FO hollow fiber membranes with thin PVDF supports with well-developed interconnected bicontinuous structures (with lower  $\tau$  values) will enable improved FO performances.

-							
Comple nome	Matariala	Thickness	$J_{ m W}$	$J_{\rm S}$	S	Pafaranaac	
Sample name	Materials	(µm)	$(L m^{-2} h^{-1})$	$(g m^{-2} h^{-1})$	(µm)	Kelefences	
PA-PVDF-A	PVDF	70	18.9	8.4	216	[This work]	
PA-PVDF-B	PVDF	180	13.8	8.2	257	[This work]	
PA-PVDF-C	PVDF	267	9.4	9.7	412	[This work]	
PA-PVDF-D	PVDF	249	9.4	10.1	413	[This work]	
PA-PVDF-E	PVDF	258	11.5	11.2	398	[This work]	
PA-PVA-PVDF	PVDF	201	10	2.6	1403	[27]	
PAN-0	PAN	100	16.6	6.5	549	[40]	
PAN-30	PAN	100	17	6	499	[40]	
PAN-60	PAN	50	24.6	19.2	305	[40]	
10 kDa	PSF	330	7.8	2.5	674	[41]	
100 kDa	PSF	300	10.3	2.2	725	[41]	
500 kDa	PSF	325	6.5	2.7	827	[41]	
dTFC-PEF	PES	300	-	-	996	[42]	
TFC-TB1	Matrimid®	215	6.3	1	1670	[43]	
TFC-TB2	Matrimid®	197	9.3	2	1110	[43]	
TFC-TB3	Matrimid®	203	9.4	2.1	1100	[43]	
TFC-FO with PES <sub>water</sub>	PES	110	32.1 <sup>*1</sup>	$6.2^{*1}$	219	[44]	
TFC-FO with PES <sub>water/NMP</sub>	PES	110	34.1 <sup>*1</sup>	$7.1^{*1}$	252	[44]	
TFC-FO with PES <sub>water/NMP/PEG</sub>	PES	110	34.5 <sup>*1</sup>	9.9 <sup>*1</sup>	261	[44]	
Toyobo-CTA	CTA	-	8	0.6	639	[45]	
PAN Modified (flat sheet)	PAN	54	$40.2^{*2}$	$1.2^{*2}$	84	[46]	
PAN Modified (flat sheet)	PAN	49	44.5 <sup>*2</sup>	11.9 <sup>*2</sup>	181	[46]	
HTI (flat sheet)	CTA	-	-	-	400 620	[2]	
Dow (flat sheet)	PSF	-	-	-	2160 9580	[2]	

Table IV.3 Comparison of FO performances of fabricated membranes with those of hollow fiber membranes reported in literature when 1.0 M NaCl was used as DS

 $^{\ast 1}$  2.0 M NaCl was used as the DS.  $^{\ast 2}$  0.5 M NaCl was used as the DS.

# **IV.4.** Conclusions

In the present study, we developed novel PVDF hollow fiber membranes with a well-developed interconnected bicontinuous structure by using HTR-NIPS, and evaluated the performances of these membranes. We then fabricated a PA active layer on the PVDF hollow fiber membranes via interfacial polymerization, and then evaluated the FO performances of the PA-PVDF composite membranes.

Investigation of the conditions for fabricating the interconnected bicontinuous structure during the phase separation process in the HTR-NIPS method showed that it is necessary to fabricate the membranes under conditions in which there is no gelation temperature and the outer coagulation solution temperature is higher than the UCST of the stock solution. We used a three-component stock solution system, i.e., PVDF/GBL/PVP, to fabricate PVDF membranes with a well-developed interconnected bicontinuous structure. These PVDF membranes, which had thicker stems in the interconnected bicontinuous structure, showed excellent PWPs and strengths, and their performances were better than those of PVDF membranes reported in the literature.

We performed interfacial polymerization on the outer surface of the hollow fiber membranes to fabricate FO membranes with a PA active layer on the outer surface. The FO performances of these membranes were then investigated in the AL-FS mode. Evaluation of the FO performances showed that  $J_w$  increased with decreasing support layer thickness *t*. There was a slight increase in  $J_w$  for the PA-PVDF membrane with the largest modal pore size and cross-sectional pore size. The estimated tortuosity  $\tau$  values for all the PA-PVDF membranes were low. Such low  $\tau$  values for all the membranes imply the formation of a well-developed interconnected bicontinuous structure; these results are consistent with the SEM images. Higher water transport was achieved when the tortuosity  $\tau$  was lower. This suggests that the interconnected bicontinuous structure of the PVDF membranes is a key factor for high-performance FO membranes.

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# **Chapter V Commercialization strategy**

# V.1. Remaining problems on commercialization

The biggest challenge to the commercialization of FO membranes is the high cost.

To assess feasibility of the FO membrane, we compared the RO membrane system (assuming that it costs ¥150,000 per membrane) and the FO membrane system (assuming a cost of ¥300,000 per membrane) (Figure V.1.). When comparing capital expense (CAPEX) and operating expense (OPEX), we found that the FO membrane system was considerably more expensive due to the high unit cost of the FO membrane module and the higher number of membrane modules on account of the lower water permeability of the FO membrane. The same reasons, namely the higher membrane exchange and amortization costs, lead to higher OPEX.

Compared to desalination systems, the FO membrane is less expensive than its competitor, the RO membrane. Thus, when attempting to commercialize FO membranes, a business strategy that acknowledges the issues associated with their costs is necessary.





Figure V.1. Cost comparing RO membrane system with FO membrane system on cost.

# V.2. Challenge to zero liquid discharge (ZLD) market

An important characteristic of the FO membrane is its high water recovery rate. Thus, we focused on the Zero Liquid Discharge (ZLD) [1] market as it could add to the economic value of these membranes.

The ZLD system recovers 80–98% of wastewater generated in industrial settings (i.e., industrial wastewater). Since it does not release wastewater into the environment, it not only prevents the pollution of natural water, but also reduces the use of freshwater in the process. Thus, this technology is widely used in inland areas with limited water resources, dry areas, and areas with severe water pollution.

The flowcharts of the ZLD system with an RO membrane (hereafter referred to as the RO/ZLD system) and the ZLD system with an FO membrane (hereafter denoted as the FO/ZLD system) are shown in Figure V.2. Conventionally, ZLD treats and recovers raw water/wastewater from a plant

via biological treatment and UF membrane filtration using the RO membrane. The water concentrated by the RO membrane is treated with a device that evaporates it. This method is called the evaporation and crystallization method. Evaporating steam is cooled to recover the evaporated water, achieving ZLD. The typical flow is seen in Figure V.2. (left side). However, since the RO membrane filters using pressure, concentrating the fluid beyond a certain level is difficult; thus, the water recovery rate of the RO membrane typically does not exceed 60–70%. However, the FO membrane, as discussed so far, is not constrained by an upper limit to its driving force, namely osmotic pressure; thus, a much higher level of concentration than the RO membrane is possible. Therefore, its water recovery rate is superior to that of the RO membrane, and it can suppress the generation of concentrated water. As a result, the amount of concentrated water flowing into the evaporation and crystallization. Using the FO membrane as the "concentration device" thus allows the evaporation and crystallization device to be miniaturized and adds to the economic value of the FO/ZLD system.



Figure V.2 Flowcharts of RO/ZLD system and FO/ZLD system

# V.3. Environmental analysis of FO/ZLD system

#### V.3.1 External environmental analysis

#### V.3.1.1 PEST analysis

In this section, we perform the PEST analysis for the external environment of the FO/ZLD system.

# (Political factors)

The ZLD system was developed in the 1970s in the US to mitigate the damage caused by salt concentrations in the effluents discharged to the Colorado River by regulating wastewater and its salt concentrations. The tightening of the wastewater regulations has helped the market growth of ZLD in inland areas, where water resources are typically limited. Globally too, wastewater regulations are being strengthened, and large ZLD market exists in the US, China, and India. To begin with, we focus on the US, where the regulation of wastewater containing heavy metals from thermal power plants was tightened by the US Environmental Protection Agency in 2017. Over 1,100 thermal power stations in the US must upgrade their wastewater facilities to meet the more stringent regulations over the next 30 years. In India, wastewater regulations have been tightened for industries, as the Ganges River is severely polluted. In recent years, the Central Pollution Control Board (CPCB) formulated ZLD guidelines for 17 industries, including fiber, pulp, paper, petrochemical, and power generation. ZLD is a must for inland power plants. In 2011, they further tightened regulations against fiber plants. In 2014, similar regulations took effect for the sugar, distillation, pulp, and paper industries. In the future, such regulations will be applied to power plants as well, likely making ZLD systems essential for inland power plants. Finally, with regard to the situation in China, petroleum and coal are being used to reduce dependence on imported energy. As such, active investments in power generation facilities that use coal and natural gas are on the rise. Approximately 70% of the electric power demand in China is met with coal gas. These facilities are located in northern China, where coal is mined, or in the inland Inner Mongolia Autonomous Region, where chronic water scarcity exists. Many coal-related industries exist in these areas, and the national policy aims to enhance and build CTX (Coal to X) industries. Specifically, in the inland areas, the construction cost of ZLD facilities is lower than the costs associated with transporting wastewater; thus, the market is expected to grow.

# (Economic factors)

The water volume forecast for the ZLD market in the next 10 years amounts to 700 million m<sup>3</sup> [2]. Based on the price of FO membranes, the estimated global market is ¥75–100 billion. The cost of desalination water recovery by ZLD is several dollars per cubic meter. Given that cost of water recovery remains high, there is no economic rationale to adopt ZLD yet; nonetheless, its uptake is imperative due to the strengthened regulations. A ZLD system consists of an RO membrane and an evaporation/crystallization system, and its operation is expensive; thus, there is a high demand for future desalination cost reductions.

#### (Social factors)

We discussed that ZLD was introduced due to tightened regulations; moreover, these regulations are backed by increasing environmental awareness globally. The CPCB decided to tighten the regulations in India because of residents protesting against the pollution of the Ganges River. Similarly, in China, the Ministry of Ecology and Environment tightened wastewater regulations because of increasing awareness about the environment and pollution, which is associated with economic development in China. Likewise, this rising environmental awareness is associated with industrial development in emerging countries, and the demand for a clean environment is expected to increase in the future as the economies of the emerging countries continue to grow. Water pollution is often attributed to population increase and urbanization, and this is also true for the inland areas.

#### (Technological factors)

Besides recovery with RO membranes, ZLD systems are also being studied in tandem with the electrodialysis (ED) method and treatment technologies using FO membranes. Nonetheless, the most widespread technology at this time is the RO/ZLD. In recent years, Companies T and M proposed developing an FO/ZLD system that uses FO membranes. However, given the slow uptake of this technology, it is unlikely that its advantages will not be realized in the near future.

Figure V.3 summarizes the above analytical results. An external environment analysis of the FO/ZLD system showed that the unit cost of the recovered water remains high for such systems, and thus, the economic rationale for its adoption does not exist at this time. However, the uptake of such systems is inevitable due to environmental regulations and social pressures. In terms of technological trends, the RO/ZLD system is the mainstream, and a technological advantage is not clear yet. Considering these facts, we predict that the number of businesses requiring such systems for wastewater treatment will increase globally, making the external environment relatively favorable for the uptake of ZLD systems. If the desalination cost of ZLD systems could be reduced compared to those of the existing systems, its social value to businesses struggling with water resources will also increase.



Figure V.3 PEST analysis results of FO/ZLD system.

# V.3.1.2 5 forces analysis

In this section, we analyzed the FO/ZLD system using five forces analysis.

#### (Threat of newcomers)

The ZLD market is not limited to water majors such as Veolia and Suez; it includes many startup companies. The above-mentioned leaders in the water market have created a niche for themselves with the existing RO/ZLD system and have completed deliveries of over 100 systems worldwide, making it the mainstream technology. On the other hand, startup companies are developing technologies to reduce the desalination cost of ZLD. For example, Saltworks Technologies and Oasys Water are creating FO/ZLD systems that utilize FO membranes. Desalitech is developing a high-energy efficiency ZLD system using an ion exchange membrane. As such, many newcomers are studying the reduction in ZLD desalination system costs. However, none of the companies have

discovered its advantage yet, as they are actively competing with each other. In the simplest sense, the ZLD system merely removes water from saltwater and crystallizes the salt as a solid. Thus, without considering the issues with system profitability, the entry hurdle is quite low. Furthermore, the concentration techniques, such as RO, FO, ED, and distillation, are diverse; thus, although there is enough room for all the organizations, the threat posed by newcomers should not be ignored.

# (Negotiation power of the buyers and threats of alternative products)

Besides the FO/ZLD system, many alternatives exist for ZLD technology, such as RO, ED, and the distillation method. Therefore, unless notable technological progress is made compared to the other methods (e.g., with regard to performance), the desalination cost of the FO/ZLD system inevitably dictates the negotiation power of the buyers and strengthens the threats posed by alternative technologies. In other words, if the desalination cost could be lowered, the negotiation power of the buyers and the threats of alternative technologies could be weakened.

#### (Negotiation power of the sellers)

The raw materials and parts for the FO/ZLD system tend to be commercially available, and unless they are unique, many suppliers can fulfil the demand, thus weakening their negotiating power.

## (Intra-industry competition)

As we have already discussed, many ZLD businesses use FO and ED rather than RO/ZLD systems. Since many ZLD technologies already exist, competition within the industry will be fierce. On the other hand, considering that the mainstream ZLD system includes RO/ZLD despite the existence of many other technologies, the desalination cost will not drastically improve. Therefore, if this cost could be reduced for the FO/ZLD system, the competition from the other technologies in the industry could be weakened.

We summarized the results of the five forces analysis in Figure V.4. Other than the negotiation power of the sellers, the ZLD market faces many barriers and consequently does not appear to be

attractive enough. However, the existing ZLD systems are not economically appealing (they were introduced solely due to regulations), and wastewater recovery is accompanied by a desalination cost of several dollars per cubic meter. Presently, the desalination cost has not been reduced despite the use of various existing technologies in the market. Therefore, the costs of many of the competing technologies are quite similar to the cost of desalination. In other words, if an FO/ZLD system with a competitive desalination cost can be developed under this environment, then buyers' negotiation power, intra-industry competition, and the threat of alternative products can be reduced, thereby increasing its appeal in the market. Below, we discuss strategies to create a cost advantage in order to increase the demand for this technology in the market.



Figure V.4 Five forces analysis results of FO/ZLD system

### V.3.2 Internal environmental analysis

#### V.3.2.1 Value chain analysis

In this section, we analyze various players in the FO membrane market using the value chain analysis. We examine the value network required to achieve competitive power in the FO/ZLD system market.

First, the FO membrane manufacturer, Company A, the DS manufacturer, Company B, and the plant manufacturer, Company C, are assessed in the value chain analysis (Figure V.5).

Company A has published several press releases on FO membranes. It reported that their FO membranes were used by a plant manufacturer. This strategy is typically followed to drive R&D, manufacturing, and sales for FO membranes. Company A produces hollow fiber RO membranes. Its strategy involves maximizing the strength of its own company along the value chain, such as their ability to manufacture FO membranes for use in similar technologies and to tap into existing RO membrane supply chains.

Next, let us discuss the analytical results for Company B. Company B differs from Company C in that it considers DSs as its major business. Thus, they commission the manufacture of DSs to an external company. They likely conduct R&D on FO membrane systems and facility designs. They have developed a value chain with DSs as the main business, but they are probably not adequately competitive.

Finally, let us focus on Company C. Company C procures FO membranes and DSs from an external source, and aims to become a plant manufacturer for FO membrane systems. However, since dealing in FO membrane systems alone was not lucrative enough, they changed their strategy to operations. Company C announced that they will start developing DSs, which likely means that they have no specific supplier.

The results of value chain analysis of each company show that all three started with different

components: FO membranes, DSs, and systems; however, none of them have achieved adequate competitiveness. The FO membrane system can provide high performance only when the FO membrane and DS are integrated with the overall system. Thus, it is difficult to establish a competitive edge by providing single elements in a value chain.

The typical value chain of a water treatment membrane shares these similarities. The weakness of these pioneering companies lies in their strategies, which are devised to cater to the value chain of existing water treatment businesses. To develop their FO membrane businesses, they should concentrate on developing FO membranes that match specific DSs instead of providing FO membranes to the existing value chain; in fact, this strategy will become the mainstream in the future, as it will allow companies to build a unique value chain. Thus, strategic collaboration with other businesses with design skills is essential for future developments pertaining to FO/ZLD systems.



Figure V.5 Value chain analysis results of FO membrane market (\*O&M = operation and maintenance)

#### V.3.2.2 VRIO analysis

The results of the VRIO analysis are also discussed here.

# (Value)

Figure V.6 shows the CAPEX calculations for RO/ZLD and FO/ZLD systems (capacity: 1000  $m^3/d$ ). In addition, Figure V.7 shows the OPEX calculations for the same systems. In this simulation, the price of the FO membrane was set at \$300,000 per membrane, while that of the RO membrane was assumed to be \$150,000 per membrane. The flow chart begins with the filtration provided by the FO and RO membranes, with a UF membrane serving as a pretreatment, followed by recycling of water with the DS in the case of the FO membrane and via RO membrane treatment in the case of the RO membrane.

First, let us consider CAPEX. When using an FO/ZLD system, the membrane-related needs are higher compared to those of the RO/ZLD system. This is because the water permeability of the FO membrane is lower than that of its RO counterpart, and more FO membranes are thus necessary compared to the number of RO membranes. Furthermore, the price per module for an FO membrane is twice as high. On the other hand, in overall terms, CAPEX of the FO/ZLD system is lower. This is because the FO membrane concentrates wastewater to a greater extent and exhibits a higher water recovery rate, which leads to the lower absolute volume of concentrated water compared to the case of the RO membrane. This aspect allows the miniaturization of the evaporation/crystallization device. Thus, overall, CAPEX of FO/ZLD systems is lower. If the performance of the FO membrane can be improved, the membrane-related cost in CAPEX could reduce as a fewer number of FO membranes would be required. Thus, its competitiveness would improve.

The same observations stand for OPEX. When using an FO/ZLD system, compared to the RO/ZLD system, the membrane-related needs are higher; as the water permeability of the FO membrane is lower than that of the RO membrane, more FO membranes are required compared to

RO membranes. This aspect, in turn, raises the costs of membrane exchange and amortization in OPEX, causing it to become higher than the corresponding value for RO membranes. However, similar to the observations made for CAPEX, FO/ZLD systems are cheaper in overall ZLD system terms. This is also because the FO membrane can concentrate wastewater better, and its water recovery rate is higher. Thus, the absolute volume of concentrated water is lower than that of the RO membrane, which greatly reduces the utility of the evaporation/crystallization device (i.e., its electricity and steam costs), miniaturizing the said device and leading to the reduction in the CAPEX and amortization cost.

The results of this cost analysis show that if FO membranes can be manufactured at a cost of less than ¥300,000 per membrane, they would become economically rational relative to the existing RO/ZLD systems. Thus, the resulting outcome for value is "YES".



Figure V.6 CAPEX comparison between RO/ZLD system and FO/ZLD system



Figure V.7 OPEX comparison between RO/ZLD system and FO/ZLD system

# (Rarity)

In the present study, the hollow fiber membrane that serves as the support layer for a polyamide is composed of PVDF. The use of polyamide FO membranes employing PVDF as the support layer was first announced in a paper by the present author. We believe that the rarity of this membrane is high, and the outcome for this part of the analysis is "YES".

# (Inimitability)

PVDF is the most commonly used raw material for existing hollow fiber membranes. Polyamide has been used as a raw material in the development of RO membranes since the 1980s. Thus, many companies around the world are conversant with the manufacturing technology. Therefore, the risk of copying post commercialization cannot be regulated. Therefore, the outcome for inimitability was determined to be "NO".

# (Organization)

We understood that the best strategy involves building a value chain for overall FO membrane systems, but since there is no such specific existing arrangement, we determined the outcome for this element as "NO".

Evaluation items				
Value	Rarity	Inimitability	Organization	Competitiveness
YES *Assuming sales at ¥300,000 per membrane				Disadvantage
YES	YES			Equilibrium
YES	YES	NO		Advantage
YES	YES	NO	NO	Sustainable advantage

Figure V.8 VRIO analysis results of FO/ZLD system

# V.3.2.2 Summary of environmental analysis

The results of the above-mentioned analysis of the prevailing environment for FO membranes in the ZLD market are summarized in the SWOT format (Figure V.9).

The internal environmental analysis showed that improving the consistency of the value chain is an effective strategy. If the price of FO membranes can be lowered, economically rational FO/ZLD systems can be achieved. The result of the external environmental analysis showed that in addition to important changes taking place in the ZLD market, ZLD is being introduced despite the lack of economic rationality by companies as part of the desalination process due to stricter regulations, and the need for reducing the desalination cost is urgent. ZLD technologies face severe competition from alternative technologies, which makes them unattractive for the current industry structure; however, if the desalination cost could be lowered, the industry structure could change.



Figure V.9 SWOT analysis results of FO/ZLD system

### V.4. Business model

As we have discussed, in order for FO/ZLD systems to provide value, it is essential to make them economically rational. The manufacturing cost per membrane remains high in small-scale production, and it is difficult to achieve economic rationality. Thus, investing in a mass production facility for FO membranes could lead to economic rationality.

We attempted a simulation for the price of an FO membrane module assuming mass production. We found that if the scale of manufacture was similar to that of the existing RO membranes, the estimated cost of the FO module could be reduced to half or even lower, thereby achieving competitiveness (Figure V.10).

In this case, FO membrane manufacture can be commercialized as a business, allowing for sufficient profits within an economically rational price range in the ZLD market.

As discussed so far, commercialization of FO membranes requires constructing a comprehensive value chain covering all elements of the FO/ZLD system. Thus, an FO membrane manufacturer and FO system seller who have engineering, procurement, construction (EPC) and operation and maintenance (O&M) functions should consider the overall unique value chain in collaboration with a business partner with the ability to build FO membrane systems. Figure V.11 shows a business model structured as a joint venture (JV). The abbreviation "JV" denotes joint investment with a business partner, wherein investment is made for mass production of FO membranes toward commercialization of FO/ZLD systems, and the manufactured FO membranes are sold accordingly. The JV serves as the assumed sales channel.

Establishing a JV with joint investment, conducting R&D consistently, and improving the competitiveness of FO membranes can help the JV to acquire a competitive advantage in the value chain analysis. From the viewpoint of VRIO as well, JVs offer a strategically advantageous position in business; thus, it is possible to achieve a sustainable competitive advantage.



Figure V.10 Relationship image between FO membrane module cost and production size



Figure V.11 Business model in FO/ZLD business

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- [2] Assessing Opportunities in the Fast-Growing Zero Liquid Discharge Market, *Lux research* (2016).

# **Chapter VI Conclusions**

In this study, we established a manufacturing technology for TFC-FO hollow fiber membranes supported by PVDF hollow fiber membranes, and formulated a business strategy for commercialization. In order to improve the FO membrane performance, we developed a new PVDF hollow fiber membrane and interfacial polymerized polyamide to obtain high FO performances. In addition, as a result of study about business strategies using FO membranes, it became clear that it is important to challenge the ZLD market by establishing a mass production joint venture for FO membranes, which has a consistent value chain from FO membrane manufacturing to plant system construction. The details of this study are summarized below.

# 1. Principle of phase separation structure control technology for porous PVDF support layer

We explored the function of the most commonly used materials, PEG and PVP, in various polymer membrane manufacturing technologies including PVDF. We assessed a PVDF/ECL/additive system to study the TIPS method.

We measured LCST, UCST, and T<sub>c</sub> and prepared a phase diagram after changing the amounts of additives PEG and PVP. The results revealed the properties of PEG and PVP.

The present study clarified the mechanisms of the polymer additives PEG and PVP in the TIPS method and showed that the phase separation structure of PVDF can be regulated by the selection of polymer additive.

# 2. Preparation of FO membrane with high strength and hydrophilic PVDF hollow fiber membrane support

We developed a new hydrophilization method that we refer to as PVA diffusion. This new method

modifies the entire surface area of a hollow fiber membrane by diffusing PVA from the bore fluid to the outer surface. This method was used to prepare a hydrophilized PVDF hollow fiber membranes (PVA-PVDF). A hydrophilized PSf hollow fiber membrane (PVA-PSf) was also prepared for reference. Interfacial polymerization was performed on the outer surface of hollow fiber substrates during the preparation of PA TFC membranes. This study examined the hydrophilicity effect that these modified support layers exert on the performance of membrane during RO and FO.

Compared with PSf membranes, PVDF membranes had higher physical strength over 10 MPa which was credited to production using a TIPS process compared with the NIPS process that is used to produce PSf membranes. The TIPS process could be useful for developing mass production techniques such as roll-to-roll processing. Comparisons of the RO test performance of hydrophilized PVDF membranes (PA-PVA-PVDF, PA-PVDF) showed that the 1,000 ppm NaCl rejection of hydrophilized support membrane was higher than that of non-modified support membranes. The FO performances were similar regardless of whether the support membranes were hydrophilized or not when measured under wet conditions. In measurements under dry conditions, however, the performance was significantly lowered in the PA-PVDF membrane that was not hydrophilized. Hydrophilization via PVA diffusion effectively produced equivalent FO membrane performances under either wet conditions.

# 3. Preparation of high performance FO membrane using a highly porous PVDF hollow fiber membrane support

PVDF hollow fiber membranes were prepared by using high-temperature rapid non-solvent-induced phase separation (HTR-NIPS). The conditions for fabricating interconnected bicontinuous structures via HTR-NIPS were investigated. We found that (1) the stock solution must not have a gelation temperature and (2) the membrane must be produced at an outer coagulation solution temperature higher than the upper critical solution temperature of the stock solution. A stock solution of PVDF/GBL/PVP that satisfied these conditions was used for successful fabrication of PVDF membranes with a well-developed interconnected bicontinuous structure. The pure water permeabilities and strengths of these PVDF membranes were higher than those of previously reported PVDF membranes. A PA active layer was prepared on the PVDF hollow fiber membranes via interfacial polymerization to obtain PA-PVDF. Investigation of FO in the active layer facing the feed solution showed that the water flux  $J_w$  increased with decreasing thickness of the support layer. Higher water transport was achieved when the tortuosity  $\tau$ , estimated from the *S* value, was lower. This suggests that the interconnected bicontinuous structure of the PVDF membrane is a key factor for FO membranes.

# 4. Commercialization strategy

We studied about FO/ZLD system in ZLD market.

The internal environmental analysis showed that improving the consistency of the value chain is an effective strategy. If the price of FO membranes can be lowered, economically rational FO/ZLD systems can be achieved. The result of the external environmental analysis showed that in addition to important changes taking place in the ZLD market, ZLD is being introduced despite the lack of economic rationality by companies as part of the desalination process due to stricter regulations, and the need for reducing the desalination cost is urgent. ZLD technologies face severe competition from alternative technologies, which makes them unattractive for the current industry structure; however, if the desalination cost could be lowered, the industry structure could change.

In order for FO/ZLD systems to provide value, it is essential to make them economically rational. We attempted a simulation for the price of an FO membrane module assuming mass production. We found that if the scale of manufacture was similar to that of the existing RO membranes, the estimated cost of the FO module could be reduced to half or even lower, thereby achieving competitiveness in the ZLD market.

To commercialization of FO membranes requires constructing a comprehensive value chain covering all elements of the FO/ZLD system. Thus, an FO membrane manufacturer and FO system seller should consider the overall unique value chain in collaboration with a business partner with the ability to build FO membrane systems.

Establishing a JV with joint investment, conducting R&D consistently, and improving the competitiveness of FO membranes can help the JV to acquire a competitive advantage in the value chain analysis. From the viewpoint of VRIO as well, JVs offer a strategically advantageous position in business; thus, it is possible to achieve a sustainable competitive advantage.

# List of publications

- Chapter II Youhei Yabuno, Kensaku Komatsu, Takuji Shintani, Keizo Nakagawa, Tomohisa Yoshioka, Functions of polymeric additives in thermally induced phase separation process of poly(vinylidene difluoride), *Membrane*, 45, 6 (2020) 324-329.
- Chapter III Youhei Yabuno, Kota Mihara, Kensaku Komatsu, Shigetaka Shimamura, Takuji Shintani, Keizo Nakagawa, Hideto Matsuyama, Tomohisa Yoshioka, Preparation of polyamide thin-film composite membranes using hydrophilic hollow fiber PVDF via the TIPS process modified by PVA diffusion, *Industrial & Engineering Chemistry Research*, 58, 47 (2019) 21691-21699.
- Chapter IV Youhei Yabuno, Kota Mihara, Naoki Miyagawa, Kensaku Komatsu, Takuji Shintani, Keizo Nakagawa, Hideto Matsuyama, Tomohisa Yoshioka, Preparation of polyamide PVDF composite hollow fiber membranes with well-developed interconnected bicontinuous structure using high-temperature rapid NIPS for forward osmosis, *Journal of Membrane Science*, 612 (2020) 118468.

# List of presentations

- Youhei Yabuno, Kota Mihara, Kensaku Komatsu, Shigetaka Shimamura, Takuji Shintani, Keizo Nakagawa, Hideto Matsuyama, Tomohisa Yoshioka, Preparation of polyamide thin film composite forward osmosis membranes using hydrophilic PVDF and PSF hollow fibers modified by PVA perdiffusion method, WeC1-5, *12th Aseanian Membrane Society (AMS12)*, Jeju, Korea, July 3rd, 2019.
- Youhei Yabuno, Kota Mihara, Naoki Miyagawa, Kensaku Komatsu, Takuji Shintani, Keizo Nakagawa, Hideto Matsuyama, Tomohisa Yoshioka, Polyamide PVDF composite hollow fiber FO membranes by high-temperature rapid NIPS, *International Congress on Membranes and Membrane Processes 2020 (ICOM2020)*, P2.004, London, UK (Online), December 8th, 2020.

# Acknowledgement

First of all, I would like to express my sincere gratitude to Prof. Tomohisa Yoshioka for the support and the opportunity to perform my research under your supervision in science and technology chapters. You spent a lot of time to discuss about this dissertation in your busy time. My technical knowledge you gave me help greatly to the future of my engineer life.

I would also like to express my sincere gratitude to Prof. Tomohisa Hasunuma for the advice to my research. You give me sincerely comments and guidance.

I would like to express my sincere gratitude to associated Prof. Keizo Nakagawa, Prof. Takuji Shintani and Prof. Hideto Matsuyama for the support and advice to progress my research in science and technology chapters.

Prof. Toru Koda, Prof. Kazuhiko Yamamoto and Prof. Ryo Shimanami for the support and the opportunity to perform my research under your supervision in commercialization strategy chapter. My business strategy knowledge you gave me help greatly to the future of my business life.

I'm deeply grateful to Kota Mihara and Naoki Miyagawa. You gave a great assistance in experiment and analysis of this dissertation.

I'm truly grateful for to Kenichi Hamada, Shigetaka Shimamura and Kensaku Komatsu. You gave great support as the boss of the company.

Finally, I'm deeply grateful to membrane and module production development department in Kuraray which gave me great understanding and support.

#### Youhei Yabuno

Graduate School of Science, Technology and Innovation

Kobe University, 2021

Doctoral Dissertation, Kobe University

"Development of polyamide thin-film composite polyvinylidene difluoride hollow fiber forward osmosis membrane and its commercialization strategy", 130 pages Submitted on January, 20th, 2021

The date of publication is printed in cover of repository version published in Kobe University Repository Kernel.

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