



Improvement of Anion Exchange Membrane Performance by Polydopamine Coating in Electrodialysis and Reverse Electrodialysis Processes

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Doctoral Dissertation

**Improvement of Anion Exchange
Membrane Performance by
Polydopamine Coating in Electrodialysis
and Reverse Electrodialysis Processes**

ポリドーパミンコーティングによる電気透析及び逆
電気透析におけるイオン交換膜の機能向上

January 2017

**Graduate School of Engineering
Kobe University**

Mahboobeh Vasselbehagh

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Mahboobeh Vasselbehagh

Graduate School of Science and Technology

Kobe University, 2017

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Chapter 1

General introduction

1.1. Outline of membrane processes

A membrane is a material used as a selective barrier between two phases. Some components are allowed to pass through the membrane into a permeate stream, whereas others are retained and accumulate in the retentate stream. In this separation process, a pressure gradient (ΔP), a concentration gradient (ΔC), an electrochemical potential gradient (ΔE), and a temperature gradient (ΔT) are used as driving forces. Fig. 1.1 shows a schematic of a membrane process.

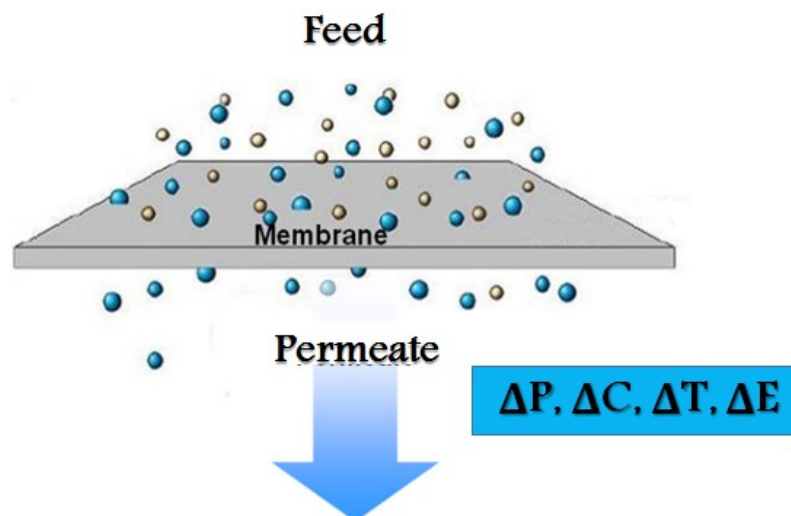


Fig. 1.1 Schematic of membrane process. ΔC , ΔP , ΔE , and ΔT indicate a concentration gradient, pressure gradient, temperature gradient, and electrochemical potential gradient, respectively, as driving forces [1].

Membrane technology is well established in separation processes. It is a feasible alternative to conventional separation methods such as evaporation and distillation. Nowadays, membrane technology is applied in many industrial processes. These applications include the following [2, 3]:

- Brackish water and/or seawater desalination for the production of potable water or high-quality industrial process water
- Waste water treatment for pollution control and/or the recovery and recycling of water and valuable waste water constituents
- Gas separation
- Natural gas sweetening
- Food and beverage processing
- Energy generation
- Selective separation at the molecular level for the production of high-value bioactive species and the manufacturing of medical, diagnostic, and analytical devices
- Regenerative medicine

Among these membrane applications, the most important are those for water treatment to deal with water scarcity and energy generation to obtain sustainable clean energy. In water treatment, reverse osmosis (RO) membranes, nanofiltration (NF) membranes, ultrafiltration (UF) membranes, and microfiltration (MF) membranes are used in pressure-driven membrane processes. Ion exchange membranes (IEMs) are used in electrochemical potential-driven processes. The pressure-driven process depending

on their pore size were shown in Fig. 1.2.

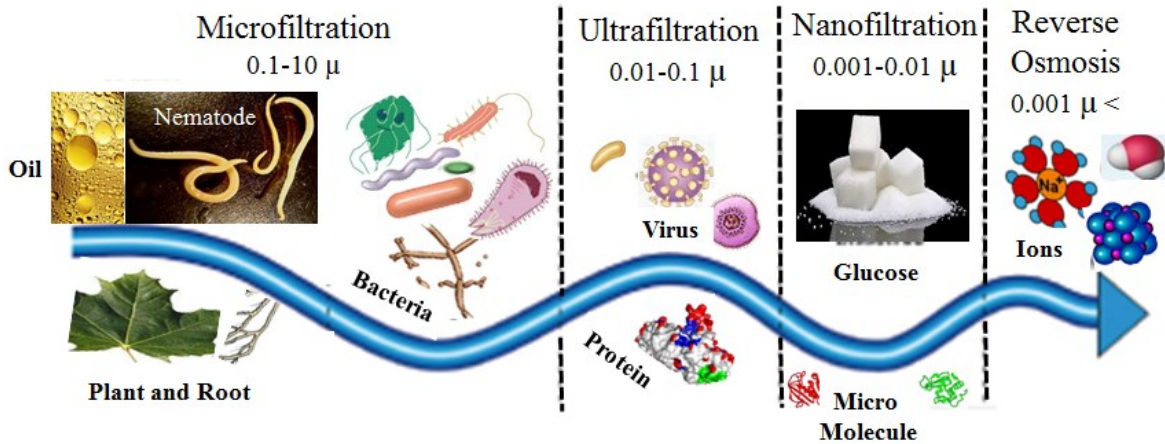


Fig. 1. 2 The relative size of different solutes removed by each class of membrane [2].

In energy generation, RO membranes (or forward osmosis (FO) membranes) are used in pressure-retarded osmosis (PRO) processes and IEMs are used in reverse electrodialysis (RED) processes. PRO is a pressure-driven process and RED is an electrochemical potential-driven process.

In this thesis, the electrochemical potential-driven processes (electrodialysis (ED) and RED), which use IEMs, are discussed. The aim is the improvement of ED and RED performance for water treatment and energy generation through surface modification of membranes. Hereafter, in this chapter, I will discuss the background and issues of these processes.

1.2. Ion exchange membranes

IEMs are key components in electromembrane processes that use an electrochemical potential gradient as a driving force. The conventional IEMs are

classified as cation exchange membranes (CEMs) and anion exchange membranes (AEMs) depending on the membrane charge. Fig. 1.3 shows the schematic of an AEM and a CEM.

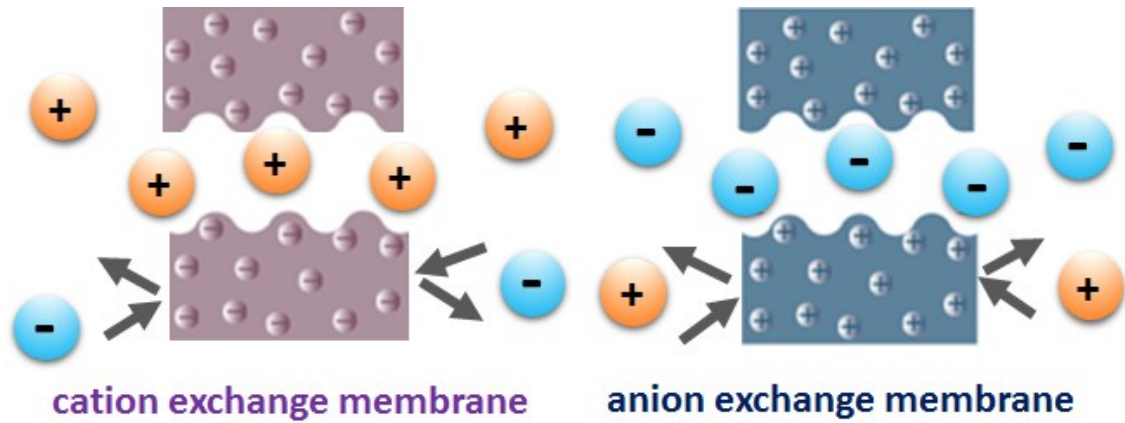


Fig. 1.3 Schematic of an AEM and a CEM.

➤ Cation exchange membranes:

These membranes contain fixed negatively charged ionic groups such as -SO_3^- , -COO^- , -PO_2^{3-} , -PHO^{2-} , -AsO_2^{3-} , and -SeO^{3-} in a polymer matrix. The fixed charge of an IEM is neutralized by counter ions (ions with a sign opposite to that of the fixed charge in the membranes). In a dry membrane, fixed ions and counter-ions are connected by ionic bonds, while in a swollen membrane, this bond is dissociated and the counter-ions are mobile and can be replaced by other ions. Thus, the membrane would be permeable to counter ions of the fixed charge. Therefore, cations (counter-ions) can permeate the CEMs, but anions (co-ions, i.e., ions with the same sign as the fixed charge in the membranes) cannot, owing to electrostatic repulsion between the anions and the membrane charge. Thus, CEMs are cation selective.

➤ Anion exchange membranes:

These membranes contain fixed positively charged ionic groups such as $-N^+HR_2$, $-N^+H_2R$, $-N^+R_3$, $-P^+R_3$, and $-S^+R_2$ in a polymer matrix. Anions (counter-ions) can permeate the AEMs, but cations (co-ions) cannot permeate through the AEMs due to electrostatic repulsion between the cations and the membrane charge. Thus, AEMs are anion selective.

The most desired properties for IEMs (CEMs and AEMs) are the following [4]:

➤ High permselectivity:

An IEM should be highly permeable to counter-ions, but impermeable to co-ions. The permeability of IEMs to the counter-ions under the driving force of an electrochemical potential gradient should be as high as possible.

➤ Low electrical resistance:

In order to reduce energy consumption in the system, the electrical resistance of the membrane should be as low as possible.

➤ Good mechanical stability:

The membrane should be mechanically strong and should have a low degree of swelling or shrinking.

➤ High chemical stability:

The membrane should be stable in the presence of oxidizing agents and over the entire pH range from 1 to 14.

➤ Low production costs

The properties of the material used to prepare the membrane, such as the density of the polymer network, hydrophobicity or hydrophilicity of matrix polymers, and type

and concentration of fixed ionic groups, determine the properties of IEMs, such as the hydrophilicity. The material properties also affect the mechanical, chemical, and thermal stability of the membrane. The type and concentration of fixed ionic charges determine the permselectivity and the electrical resistance of the membrane. It is difficult to optimize the properties of IEMs because the parameters that determine their properties often act contrary to each other. For instance, a high concentration of fixed ions in the membrane matrix leads to low electric resistance but causes a high degree of swelling and poor mechanical stability. A high degree of polymer cross-linking improves the mechanical strength of the membrane but also increases its electrical resistance.

The physical properties of some commercially available IEMs prepared by different companies are listed in Table 1.1.

Table 1.1 Physical properties of some commercially available IEMs [5].

Membrane	Structure Properties	IEC (meq/g dry-membrane)	Thickness (mm)	Water Content (%)	Area Resistance $^*(\Omega \text{ cm}^2)$	Perm-selectivity $^{**}(\%)$
Astom Corporation, Japan						
Neosepta CMX	Cation, PS/DVB	1.5–1.8	0.14–0.20	25–30	1.8–3.8	97
Neosepta AMX	Anion, PS/DVB	1.4–1.7	0.12–0.18	25–30	2.0–3.5	95
Neosepta CMS	Cation, PS/DVB	2.0	0.15	38	1.5–2.5	-
Neosepta ACM	Anion, PS/DVB	1.5	0.12	15	4.0–5.0	-
Asahi Glass Co. Ltd., Japan						
CMV	Cation, PS/DVB	2.4	0.15	25	2.9	95
AMV	Anion, PS/butadiene	1.9	0.14	19	2.0–4.5	92
HJC	Cation, Heterogeneous	1.8	0.83	51	-	-
Ionic Inc., USA						
61CZL386	Cation Heterogeneous	2.6	0.63	40	9	-
103PZL183	Anion Heterogeneous	1.2	0.60	38	4.9	-
Dupont Co., USA						
Nafion 117	Cation Fluorinated	0.90	0.20	16	1.5	97
Nafion 901	Cation Fluorinated	1.1	0.4	5	3.8	96

RAI Research Corp., USA						
R-5010-H	Cation LDPE	0.9	0.24	20	8.0–12.0	95
R-5030-L	Anion LDPE	1.0	0.24	30	4.0–7.0	83
R-1010	Cation	1.2	0.10	20	0.2–0.4	86
R-1030	Fluorinated	1.0	0.10	10	0.7–1.7	81
	Anion Fluorinated					
Institute of Plastic Materials, Moscow						
MA-40	Anion	0.6	0.15	17	5.0	95
CSMCRI, Bhavnagar, India						
IPS	Cation LDPE/HDPE	1.4	0.14–0.16	25	1.5–2.0	97
IPA	Anion LDPE/HDPE	0.8–0.9	0.16–0.18	15	2.0–4.0	92
HGC	Cation PVC, Het	0.67–0.77	0.22–0.25	14	4.0–6.0	87
HGA	Anion PVC, Het	0.4–0.5	0.22–0.25	12	5.0–7.0	82

IEC: Ion exchange capacity; PS: Polystyrene; DVB: Divinyl benzene; LDPE: Low-density polyethylene; HDPE: High-density polyethylene; PVC: Polyvinyl chloride. *0.5 M NaCl at 25 °C. **0.1/0.001 M NaCl.

1.3. Water treatment

1.3.1. Water scarcity

As mentioned above, potable water production through desalination of seawater, brackish water, and other water sources is the largest and most important application of ED processes. Currently, one of the most serious global problems is water scarcity, even though 71% of the Earth's surface is covered by water. According to the International Water Management Institute (IWMI), 30% of people in the world are endured by water scarcity [6]. Approximately 25% of the world's population lives in areas where water is physically scarce. More than one billion people live in areas where water is economically scarce, or where water is available in rivers and aquifers, but the infrastructure required to make this water available to people is lacking. Most of the Earth's water (97%) is in seas and oceans and has high salinity. Thus, these water sources obviously cannot be used as sources of drinking water without some treatments and desalination. As shown in Fig. 1.4, only 3% of water is fresh water. However, fresh

water includes water from icecaps and glaciers (68.7%) and groundwater (30.1%), which is not easily available and is sometimes polluted by human activities [7-9].

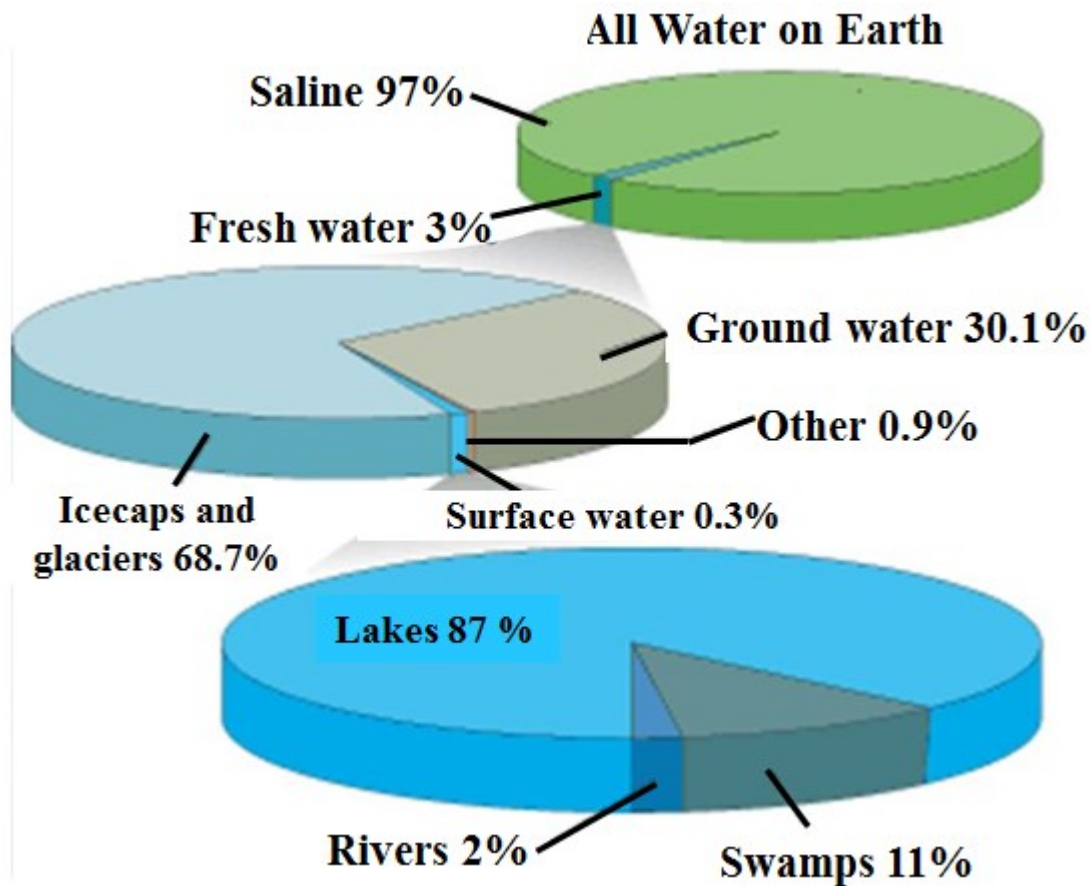


Fig. 1.4 Distribution of the Earth's water [10].

One significant cause of water scarcity is agriculture, since crop production requires up to 70 times more water than the amount used for drinking and other domestic purposes. The IWMI estimates that every 4.184 J from food requires approximately 1 L of water to produce. Such unsustainable consumption has led to

localized areas of water scarcity and has significantly altered freshwater ecosystems. Recycled water can be used to satisfy water demands in numerous applications such as agriculture and landscape irrigation, industrial processes, toilet flushing, or groundwater basin replenishment depending on the level of treatment [11]. The total amount of recycled water used in Japan in 2010 was approximately $2.5 \times 10^8 \text{ m}^3$. Fig. 1.5 shows the volume of recycled water used in Japan for various purposes [12]. In addition, water produced from oil and natural gas processing and from salt water could be used to overcome the water shortage problem [13].

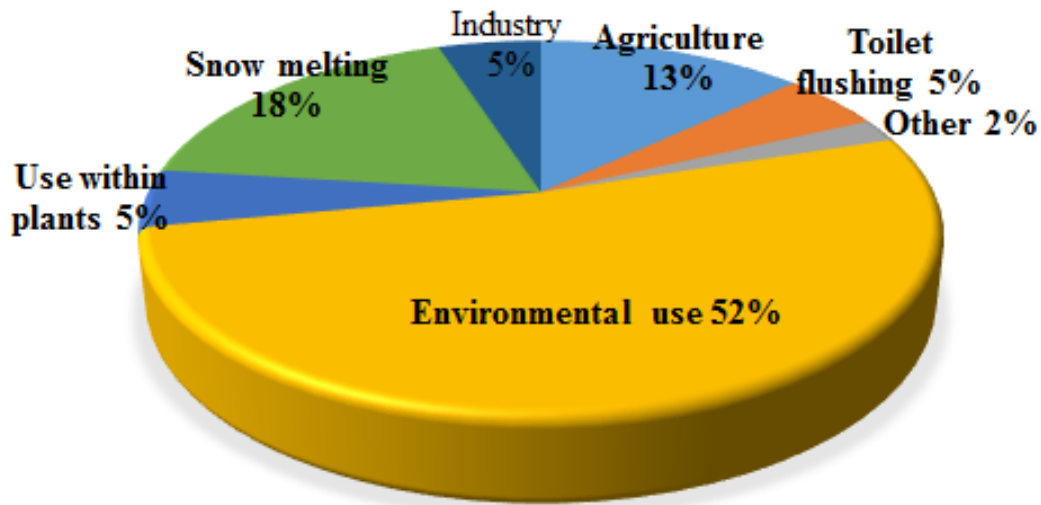


Fig. 1.5 Relative volumes of recycled water used in Japan for various purposes [12].

1.3.2. Electrodialysis

There are several electrochemical potential-driven processes, such as ED (potable water production) and ED with bipolar membranes (acid and base production from salts).

Among them, the important process for water treatment is ED. ED is an electrochemical separation process in which IEMs (CEMs and AEMs) are arranged alternately in a direct electric current (DC) field. The principle of ED was developed more than one century ago by Ostwald in 1890 and demonstrated for the first time by Maigrot and Sabates in the same year with the initial aim of demineralizing sugar syrup [14, 15]. ED has developed since 1890, and its developmental milestones are shown in Fig. 1.6.

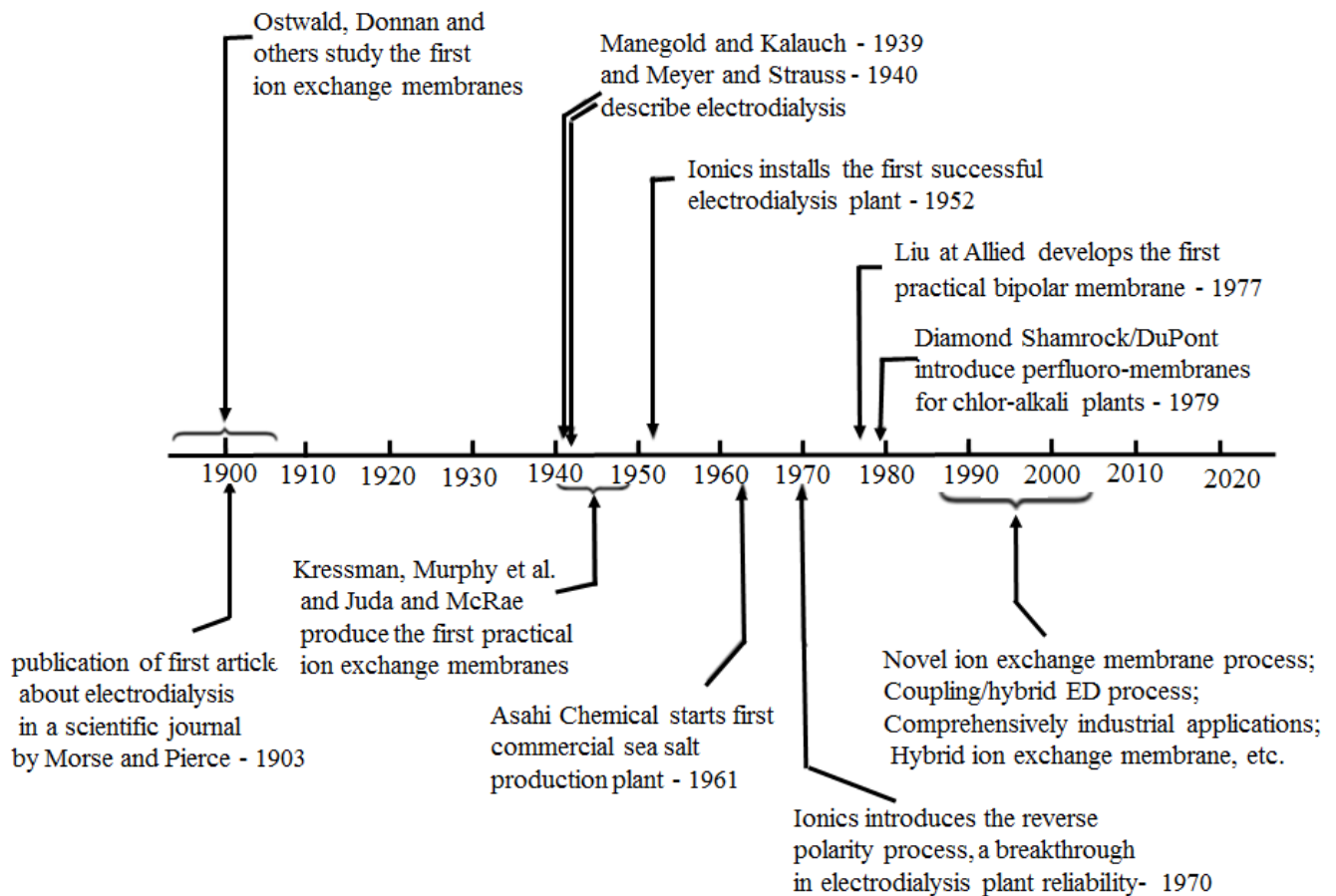


Fig. 1.6 Milestones in the development of IEM processes [2, 16].

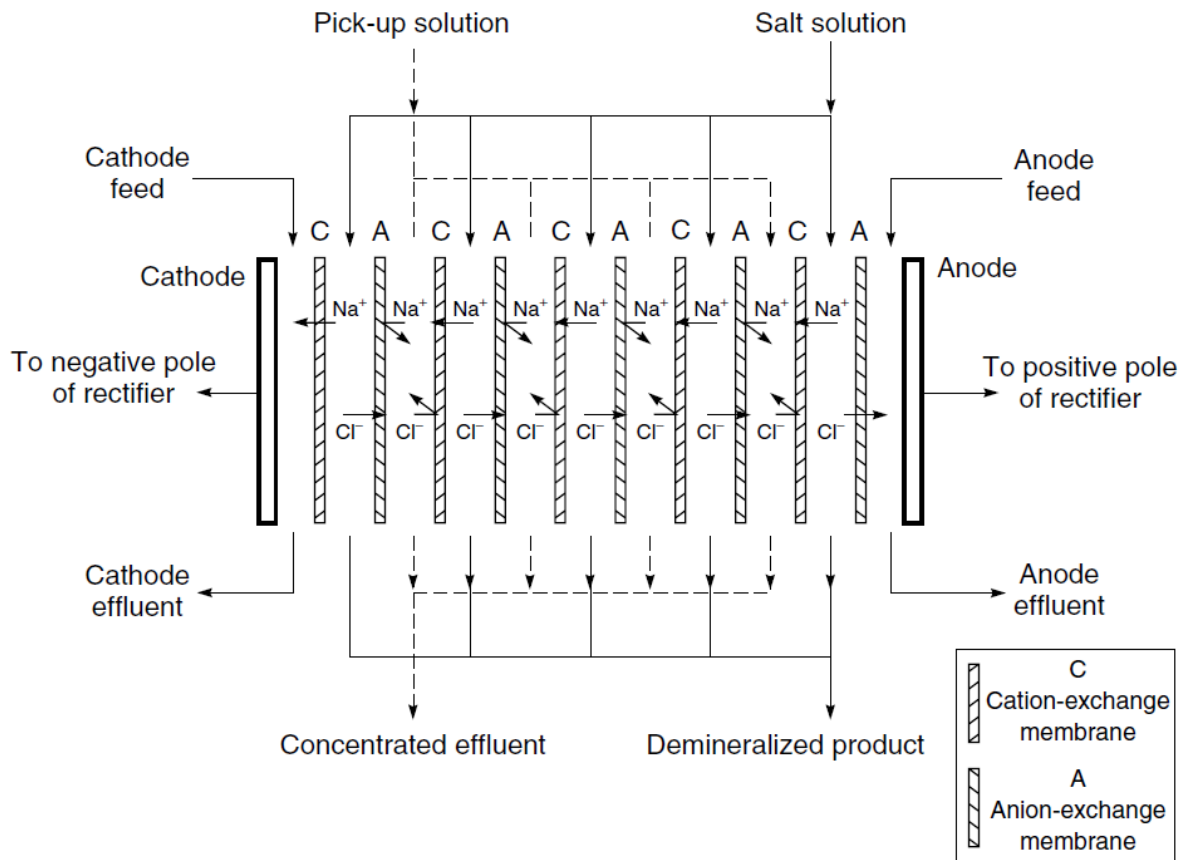


Fig. 1.7 Schematic diagram of an electrodiolysis stack. Alternating cation and anionpermeable membranes are arranged in a stack [2].

Fig. 1.7 shows the fundamental ED system, where C denotes a CEM and A denotes an AEM. In an ED system, the feed solution is divided by the pairs of AEMs and CEMs. Anions migrate towards the anode through the AEMs via externally applied DC voltage, while cations migrate to the cathode through the CEMs. However, anions cannot permeate the CEMs and cations cannot permeate the AEMs because of the electric repulsion between the ions and the membrane charge. Consequently, the ion concentration in some compartments between AEMs and CEMs decreases and desalination occurs. Those compartments are called the “dilute compartments.” At the same time, the ion concentration increases in the compartments next to the dilute compartments, and therefore, these compartments are called the “concentrate

compartments.” Fig. 1.8 shows an ED plant in which 100–200 cell pairs are arranged between the electrodes in one stack.



Fig. 1.8 An electrodesalination plant [4].

The advantages of ED over RO and NF are the following [4, 17]:

- High water recovery rates due to lack of osmotic pressure limitations
- Very low requirement of feed pretreatment in water desalination since membrane fouling and scaling is reduced to a minimum by reverse polarity operation (i.e. electrodesalination reverse (EDR))
- Long useful lifetime of membranes that is related to higher chemical and mechanical stability

- Possibility of operation at temperatures up to 50 °C
- Simple start-up and shut-down of the process for intermittent operation

1.3.3. Electrodialysis issues

1.3.3.1. Membrane permselectivity

Potable water production via desalination of brackish water sources is the largest and most important application of ED. One of the most important properties of IEMs is the permselectivity for specific ions in the production of potable water with ED processes. In particular, the monovalent anion selectivity of AEMs is very important. A high selectivity for monovalent anions (relative to multivalent anions) assists to improve two properties:

- Remove harmful ions with high current efficiency:

Harmful anions such as NO_3^- and F^- should be removed to make water safe and potable

- Prevention of inorganic fouling by reducing scale formation:

Multivalent anions like SO_4^{2-} are removed from feed solutions since AEMs are generally multivalent-anion selective. With increased multivalent anion concentrations in the concentrate compartment, precipitation of insoluble materials such as calcium sulfate (CaSO_4), which is known as scaling, takes place and ED performance decreases.

Thus, to enhance ED performance, improvement of the monovalent anion selectivity of AEMs is required.

In general, permselectivity is described with a transport number ratio between the

target ion and a standard ion. The chloride ion is commonly considered as the standard ion. If am represents the target anion and an represents the standard anion, then the transport number ratio between am and an , P_{an}^{am} , is defined by Eq. (1.1) [18]:

$$P_{an}^{am} = (t_{am}/[am]_B)/(t_{an}/[an]_B) = (J_{am}/J_{an})([an]_B/[am]_B) \quad (1.1)$$

Here, t_{am} , $[am]_B$, and J_{am} denote the transport number, concentration (eq/m³), and flux (eq/m²s) of the target anion (am), respectively; t_{an} , $[an]_B$, and J_{an} denote the transport number, concentration (eq/m³), and flux (eq/m²s) of the standard anion (an), respectively. As shown in Eq. (1.1), the transport number is divided by the concentration, since the transport number depends on the concentration. Thus, P_{an}^{am} represents the transport number ratio per unit concentration and is obtained from the ion fluxes and concentrations in the dilute compartment. An AEM is target-ion selective if P_{an}^{am} is greater than 1 and standard-ion selective if P_{an}^{am} is less than 1.

1.3.3.2. Concentration polarization and limiting current density

One of the important problems in ED processes is concentration polarization, which is due to a difference between the transport number of a counter-ion in a bulk solution and that within a membrane. The counter-ion concentration at the IEM/bulk solution interface in a dilute compartment decreases depending on the electric current density that flows through the IEM. This phenomenon is called concentration polarization, and negatively affects the ED system. The transport number of counter-ions in an IEM is generally close to 1 and that of the co-ions is close to 0. At the IEM surface that faces the dilute solution, the concentration of the counter-ions is reduced since their transport number in the bulk solution is lower than that in the membrane.

This results in a reduction of the electrolyte concentration at the dilute bulk solution/IEM interface, and concentration polarization occurs at the membrane/bulk solution interface. On the other hand, the electrolyte concentration increases at the IEM/concentrated solution interface. The salt concentration profiles and the fluxes of the cations and anions in the concentrated and dilute solutions at the surface of a CEM are shown in Fig 1.9. In this figure, J represents the ion fluxes and C represents the concentration profiles on both sides of a CEM. The superscripts mig and diff refer to migration and diffusion, the superscripts d and c refer to the dilute and concentrate solution, and the superscripts b and m refer to the bulk phase and membrane surface, respectively. The subscripts a, c, and s refer to anion, cation, and salt, respectively.

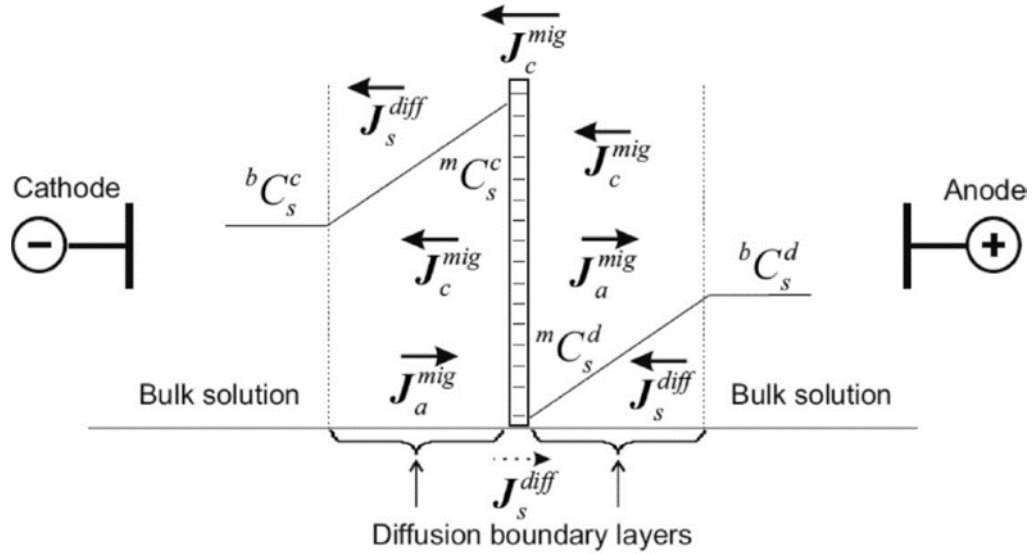


Fig. 1.9 Schematic drawing illustrating the concentration profiles of a salt in the laminar boundary layers on both sides of a CEM and the flux of ions in the bulk solutions and the membrane [17].

Due to concentration polarization, the salt concentration in the concentrate compartment exceeds the solubility, which can result in precipitation of the salt. In the dilute side, concentration polarization leads to the depletion of ions at the membrane surface and determines the limiting current density, which is the current density when the ion concentration at the membrane surface approaches zero. As a result, there are no salt ions to carry an electric current and water dissociation occurs.

Fig. 1.10 shows the current through an ED stack as a function of the applied potential. As shown in this figure, the curve is divided into three regions:

I) Under limiting current density region:

When counter-ions migrate to the anode and cathode through the IEMs during ED operations, the current density increases linearly with the applied voltage based on Ohm's law, since system resistance is constant.

II) Limiting current density region:

The ion concentration at the IEM/bulk solution interface decreases in the dilute compartment. Consequently, electrical resistance increases. Even though the applied voltage increases, the electric current increases slightly and remains almost constant.

III) Over limiting current density region:

At a certain applied voltage, water dissociation takes place and H^+ and OH^- ions are produced at the membrane/bulk solution interface. These ions carry the electric current and the current density increases sharply.

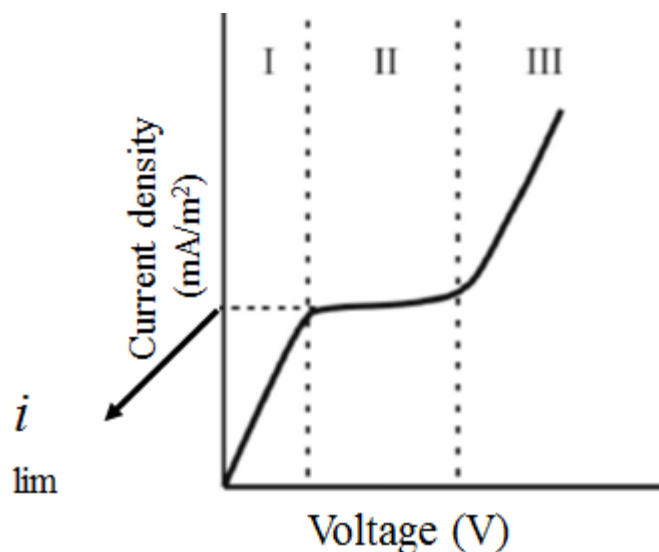


Fig. 1.10 Schematic drawing of a current versus voltage curve of an ED stack. i_{lim} indicates the limiting current density.

The limiting current density depends on the bulk electrolyte concentration, agitator efficiency, and membrane properties. Ions partitioned into the membrane from the dilute compartment carry the electric current. Thus, the limiting electric current density depends on the bulk concentration in the dilute compartment. The limiting current density for the commercial homogeneous AMX membrane is 13.9 mA/cm² for 0.1 M NaCl and 0.7 mA/cm² for 0.005 M NaCl [19]. In an ED system, electrolytes permeate from the dilute compartment to the concentrate compartment through IEMs. The dissociation of water and generation of H⁺ and OH⁻ lead to a decrease in the pH in the dilute solution and an increase in the concentrated solution when the electric current exceeds the limiting electric current density.

1.3.3.3. Fouling

1.3.3.3.1. What is the fouling phenomenon?

It is well known that fouling is a serious problem that faces all membrane

separation processes, including IEM processes such as ED and RED. Fouling is the result of interaction between a membrane and materials called foulants in the feed solution, like humic acids, surfactants, and biological materials. Fouling seriously affects membrane performance in the following ways [20]:

- Increases membrane resistance and energy consumption
- Shortens membrane life
- Increases operating cost

Therefore, it is needed to improve anti-fouling properties to enhance the IEM processes performance. Fouling, as interaction between a foulant and a membrane surface, depends on the membrane properties (hydrophilicity, charge density, and membrane surface roughness) [21, 22], operation conditions (temperature, flow rate), and the foulant materials [23, 24].

1.3.3.3.2. Fouling classification

Membrane fouling is often classified according to the foulant substance. Foulants are classified as non-living substances (organic fouling, inorganic fouling (scaling)) or living organisms (biofouling (i.e., biofilm formation)).

- Inorganic fouling (scaling):

Inorganic fouling is the result of precipitation of an insoluble inorganic material onto a membrane surface (e.g., iron or manganese oxides, CaCO_3 , CaSO_4 , silica, and $\text{Ca}_3(\text{PO}_4)_2$) [25].

➤ Organic fouling:

Organic fouling is the adsorption of dissolved organic compounds (e.g., humic acids, oils, carbohydrates, detergents, and proteins) on a membrane surface [26].

➤ Biofouling:

Biofouling (biofilm formation) is the accumulation of microorganisms (e.g., bacteria) on a surface due to deposition and/or growth. Biofilms typically develop in five stages as shown in Fig. 1.11 [27, 28].

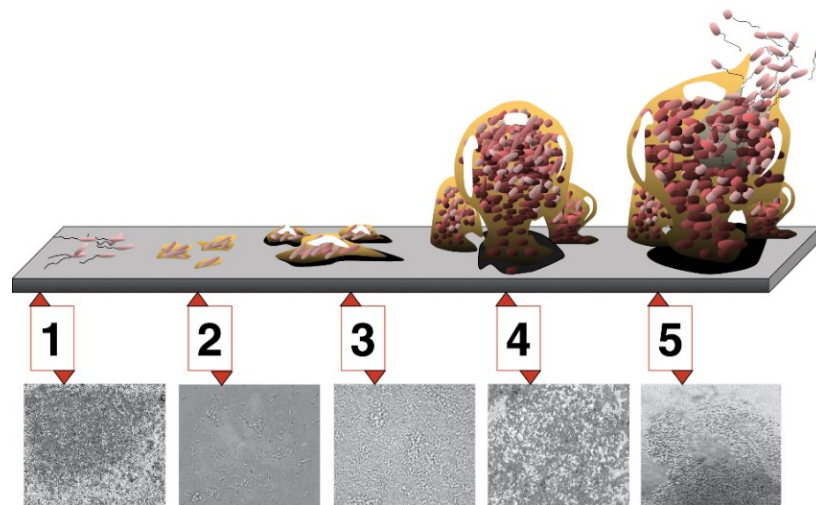


Fig. 1.11 Illustration of the five stages of biofilm formation: stage 1, initial attachment; stage 2, irreversible attachment; stage 3, maturation I; stage 4, maturation II; stage 5, dispersion. Each stage of development in the diagram is paired with a photomicrograph of a developing *Pseudomonas aeruginosa* biofilm [27].

1.3.3.3.3. Fouling evaluation

Numerous methods and apparatuses have been used to assist in the study of membrane fouling. Membrane fouling can be detected using direct or indirect methods.

➤ Direct method:

This method involves microscopy inspection of an exposed membrane surface

using techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and confocal laser scanning microscopy (CLSM). For example, it is possible to observe the bacteria and to distinguish between living and dead bacteria adhered on a membrane surface with a CLSM apparatus (refer to chapter 5). Fig. 1.12 shows SEM images of an AEM membrane (NEOSEPTA AMX, Astom Corp.) (a) before and (b) after adhesion test. The membrane was immersed into *P. putida* (O.D.₄₅₀: 0.5) for 20 h [29].

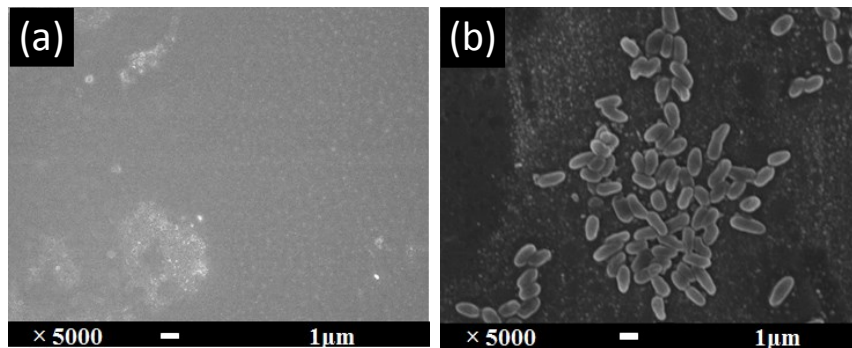


Fig. 1.12 SEM images of an AEM membrane (A NEOSEPTA AMX (Astom Corp.)) a) before and (b) after adhesion test. The membrane was immersed into *P. putida* suspension (O.D.₄₅₀: 0.5) for 20 h [29].

➤ Indirect method:

Fouling formation can be detected indirectly by measuring the parameters related to membrane performance.

In this study, I examined membrane surfaces using SEM and CLSM as direct methods and measured the potential difference across the membrane as an indirect method to explore the organic fouling and biofouling potentials of AEMs in ED processes (chapters 4 and 5). In addition, SEM image was used as a direct method and

the decreases in the generated currents in RED processes were measured as an indirect method to evaluate the biofouling of AEMs (chapter 6).

1.3.3.3.4. Membrane properties that affect fouling

Some properties significantly influence membrane fouling. Most fouling-prevention strategies focus on controlling these properties to improve anti-fouling properties. These properties are as follows:

➤ **Surface hydrophilicity:**

It is generally accepted that an increase in hydrophilicity results in better fouling resistance, because proteins, bacteria, detergents, and many other foulants are hydrophobic in nature. An increase in hydrophilicity leads to decrease hydrophobic interaction between foulants and the membrane surface. A hydrophilic surface has an inherent ability to form a hybrid layer (water layer) with surrounding water molecules and prevent fouling [30].

➤ **Surface charge density:**

In general, a repulsive force between a charged surface and charged foulants prevents foulant deposition on the membrane surface and reduces fouling. For example, increasing the negative charge density of an AEM surface improves anti-organic fouling properties, anti-inorganic fouling properties, and anti-biofouling properties [29]. Improvement of anti-fouling properties is described in chapters 3, 4, and 5 in detail.

➤ Surface roughness:

Fouling is more serious for rougher surfaces, and this is attributed to the enhancement of interactions between foulant particles and membrane surface [31]. Foulant particles accumulate in the valleys of rough surfaces. As a result, the valleys become blocked, and fouling becomes more severe for rougher membrane surfaces. Adhesive forces (interactions between foulant particles and a membrane surface and interactions between foulant particles) are most probably the important factors for fouling. In addition, membranes with smooth surfaces show high surface charge densities and high surface hydrophilicity, which lead to good anti-fouling properties [32].

For biofouling, the following two types of properties have been discussed thoroughly:

➤ Anti-adhesion properties:

Anti-adhesion properties increase the adhesion resistance of a surface against attachment of bacteria. Approaches to enhance anti-adhesion properties have involved improving the hydrophilicity and negative charge density of a membrane surface and also decreasing surface roughness. Thus, surface modification methods such as coating are being used to improve anti-adhesion properties [31, 33].

➤ Anti-microbial properties:

Anti-microbial properties improve bacteria lysis. These properties can be divided into two categories:

➤ Contact killing:

Contact killing is based on direct contact between a biocide and the bacteria cell. In this approach, the membrane surface is functionalized with anti-biotic groups. These include anti-microbial peptides, which are usually positively charged compounds. The positive charges can theoretically penetrate a bacterial cell membrane, which disrupts its integrity and induces cell lysis. Some examples of these compounds are quaternary ammonium salts, phosphonium salts, and chitosan [34, 35].

➤ Biocide leaching (release killing):

In release killing, ions are released from a biocide material and come into contact with and kill bacteria. This is one of the oldest methods to disinfect drinking water; it has been employed since ancient times using silver or copper [36]. Fig. 1.13 shows a schematic of the main approaches to prevent biofouling.

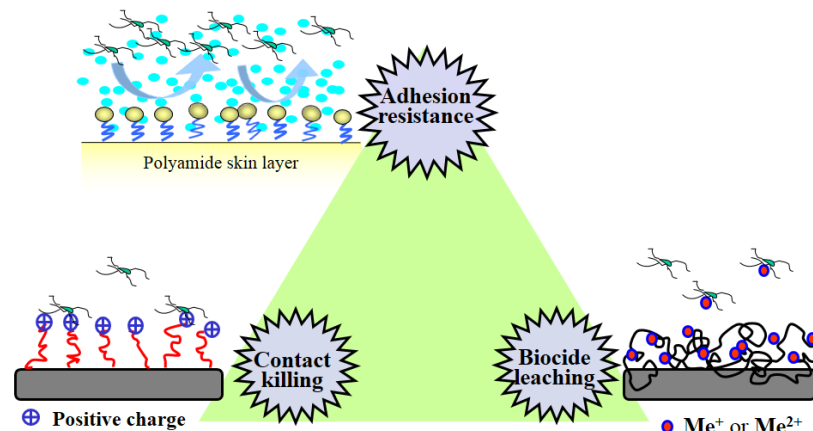


Fig. 1.13 The main approaches for controlling biofouling [34].

1.3.3.3.5. Strategies to improve anti-fouling properties

1.3.3.3.5.1. Membrane modification

As already discussed, it is well known that fouling mainly depends on membrane properties such as hydrophilicity, roughness, and surface charge density. Membrane modification is a promising method to improve these properties. In particular, for commercially available membranes, membrane modification methods such as coating, blending, and grafting are the approaches to improve anti-fouling performance. In this section, these methods are summarized briefly.

➤ *Coating*

Coating is the simplest and most popular method to improve the anti-fouling potential of a membrane surface. In this method, coating materials attach to the substrate through covalent or non-covalent bonding and form a thin layer. The following are common coating methods:

➤ Monolayer formation on a membrane surface:

A polyanion or polycation monolayer that is chemically deposited on a membrane surface improves membrane properties (e.g., IEM modification with poly(sodium 4-styrene sulfonate) (PSS)) [37].

In this study, the monolayer coating method was applied and polydopamine (PDA) was successfully coated on an AEM, resulting in improved ED performance. PDA formed a tight layer on the membrane surface through strong covalent and/or non-covalent interactions with the substrate [38]. It is well known that PDA is a super-hydrophilic material that increases the hydrophilicity of hydrophobic surfaces such as

polyethylene (PE), poly(vinyl fluoride) (PVDF), and polytetrafluoroethylene (PTFE) [39, 40].

➤ **Layer-by-Layer (LbL) method:**

Self-assembly of alternating cationic and anionic polyelectrolytes is an approach to assembling nanometer-scale multilayers on solid surfaces to modify a membrane surface. The LbL method involves adsorption of oppositely charged species from aqueous media onto a solid surface. The LbL method improves the anti-fouling potential of a membrane surface by increasing the hydrophilicity and surface charge density [41].

➤ ***Grafting***

The grafting technique has been widely applied to produce anti-fouling surface layers. Several common techniques can be used to initiate grafting, including (I) chemical techniques, (II) photochemical techniques and/or those that employ high-energy radiation, (III) techniques involving the use of a plasma, and (IV) enzymatic techniques. The selection of a suitable grafting technique depends on the chemical structure of a membrane and the desired characteristics of the modified surface [42]. One of the emerging strategies for creating bacteria-resistant surfaces is to use hydrophilic polymers or polymer segments that are capable of forming strong hydrogen-bonding interactions with water. For example, poly(ethylene glycol) (PEG) immobilized or grafted onto a surface forms a highly hydrated layer that significantly reduces the adsorption of proteins and bacteria owing to its strong affinity for water molecules [43].

➤ ***Blending***

In the blending method, two or more polymers are physically mixed to achieve the required properties. The blending of hydrophobic polymers with hydrophilic polymers such as poly(vinylpyrrolidone) (PVP) has been widely applied to increase the hydrophilicity of membrane surfaces and improve anti-fouling properties [44].

1.3.3.3.5.2. Electrodialysis reversal

Electrodialysis reversal (EDR) is an ED operation specific strategy to improve anti-fouling properties of IEMs in ED processes. Fouling problems in ED processes have been sufficiently reduced by using EDR [45]. The principle of EDR is illustrated in Fig. 1.14. When an electric current is applied to an ED system, a negatively charged foulant will migrate to the AEM and be deposited on the membrane surface, and form a fouling layer. When the polarity is reversed at certain times, the anode is converted to the cathode and vice versa. Thus, the negatively charged components will migrate from the AEM back into the feed stream and the membrane properties will be restored. The dilute and concentrate compartments are also reversed by automatic valves that control the flows in the stack (i.e., the dilute cell will become the concentrate cell and vice versa). This technique is also called “clean in place.”

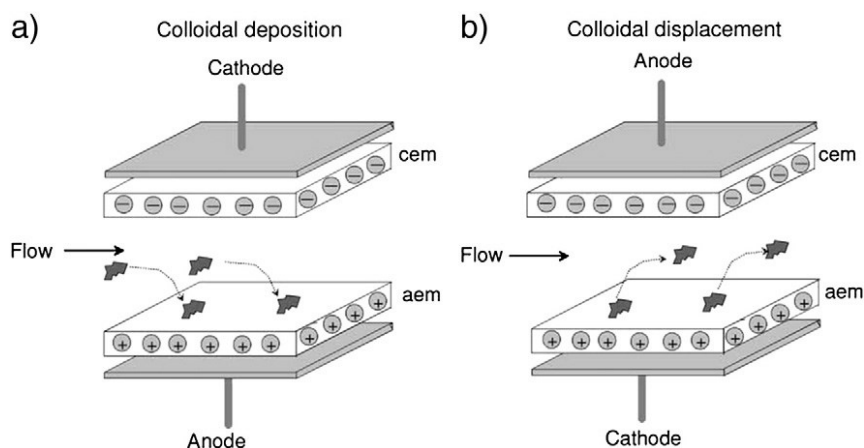


Fig. 1.14 Schematic drawing illustrating the removal of deposited negatively charged colloidal components from the surface of an AEM [4].

1.3.3.3.6. CEM fouling

In an ED system, since CEMs have negative fixed charges, organic fouling and biofouling are not serious problems. However, CEMs are significantly affected by inorganic fouling (scaling) [46]. Research has shown that scaling can become a severe problem especially in the presence of calcium and carbonate species [47, 48]. In a natural environment, negatively charged species, like hydroxide or carbonate species, adsorb onto the surface of CEMs. When divalent cations like Ca^{2+} or Mg^{2+} are transported through the membranes, they react with the negatively charged species to form insoluble scale and adsorb on the membrane surface. It is obvious that the methods used for AEMs such as the application of a polyanion coating layer are not applicable to CEMs, since applying a positively charged coating layer onto a CEM would only exacerbate the fouling problem. However, nanocomposite CEMs (i.e., combinations of polymers and inorganic or organic nanomaterials) have been found to be effective for reducing fouling, because incorporation of functionalized inorganic fillers increases

both the density of the negative charges on the surface and the hydrophilicity. Examples include the combination of oxidized multi-walled carbon nanotubes (O-MWCNTs) as an inorganic nanomaterial with sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) and or combination of SPPO with iron oxide [49, 50]. An increase in the surface charge density results in an increase in electrostatic repulsion between a membrane surface and negatively charged species, which reduces the likelihood of anion adsorption. Increasing membrane hydrophilicity also enhances the anti-fouling properties of a membrane because most foulants are hydrophobic. However, an optimal loading (i.e., filler concentration) should be considered in nanocomposite membranes to ensure that the surface morphology does not change and that the surface roughness does not increase.

1.3.3.3.7. AEM fouling

Organic fouling and biofouling are more severe on AEMs than on CEMs. Whereas AEMs have positive fixed charge and most of foulants, such as surfactants, humic acids, proteins, and bacteria, have negative charges. However, the high multivalent anion permselectivity of AEMs also leads to inorganic fouling and membrane scaling. This issue is described in chapter 3 in detail. Research on ED processes has shown that organic fouling and biofouling can become serious problems especially in the desalination of sea water and drinking water treatment. When negative organic foulants (e.g., sodium dodecyl benzene sulfonate, SDBS) and/or biofoulants (e.g., *P. putida*) are adsorbed on a surface, a fouling layer is formed. Fouling of AEMs can be reduced by improving some membrane properties such as hydrophilicity and negative-charge

density on the membrane surface [37, 41, 51]. Applying a negatively charged coating layer onto the AEMs would enhance these properties. However, there is a trade-off to consider between these two properties, hydrophilicity and surface charge density, and surface roughness when applying a coating layer. It has been reported that membranes with rougher surfaces trap foulants more easily, and thus are fouled faster [52]. Therefore, an optimal concentration of the coating layer is required in a modification method in order to minimize membrane fouling.

1.4. Sustainable energy

1.4.1. Lack of fossil energy sources

As already mentioned, sustainable energy generation is an important membrane application. The limited sources of fossil fuels, such as oil, coal, and natural gas, have led to increased energy demands, CO₂ emissions, and air pollution, and global warming has led to the demand for energy generation from sustainable and renewable sources. Fig. 1.15 shows the global fossil fuel production and the forecast for these energy sources.

The oceans are the largest untapped renewable energy resource that can provide clean and sustainable energy. Oceans and surface waters have the potential to contribute salinity gradient energy, thermal energy, and energy generated by waves and tidal forces. Mixing two water streams with different salt concentrations (e.g., sea and river water) have potential to generate salinity gradient energy (SGE). SGE is the second-largest marine-based form of energy, with an estimated global power production potential of

2.4–2.6 TW. SGE is based on membrane technology. There are two main techniques for extracting energy from a salinity gradient: pressure-retarded osmosis (PRO) and reverse electrodialysis (RED).

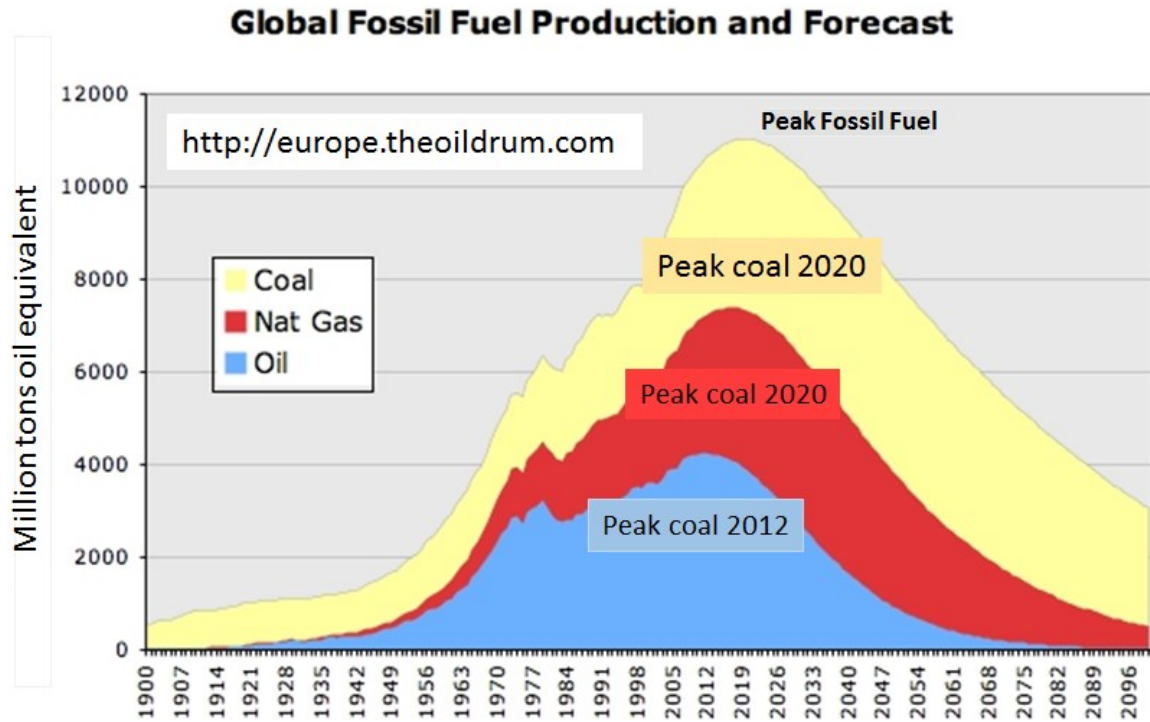


Fig. 1.15 Global fossil fuel production and forecast [53].

1.4.2. Reverse electrodialysis processes

RED system is an electrochemical process based on a membrane and a dialytic battery. The stack design of RED is essentially the same as that of an ED process. In an RED process, the cells (containing an AEM and a CEM, and low and high salinity water compartments) are also arranged alternately between two electrodes. However, the input

and output are opposite to those of ED. In ED, the input is an electric current and the outputs are low and high salinity water. In contrast, in RED, the inputs are low and high salinity water and the output is an electric current. Fig. 1.16 shows a schematic of an RED system. Electric power is obtained when the membrane stack potential exceeds the redox potential at the electrodes and a current is generated. Anions migrate to the anode through the AEM and cations migrate to the cathode through the CEM under an electrochemical potential gradient. The ionic current is converted into an electric current owing to the redox reaction at the electrodes. An electron is released at the anode side owing to an oxidation reaction. Subsequently, the electron is transported through an external circuit containing an external load to the cathode side. This electron is accepted at the cathode side by reduction reaction and energy is generated [54-57].

The principle of RED was first developed in 1954 by Pattle. He was the first to be able to generate power through the selective transport of ions by mixing fresh and salt water [58]. Further development was done by Weinstein and Leitz in the late 1970s [59]. In the early 1980s, Lacey reported that membranes for RED processes should have low electrical resistance in order to achieve high power outputs. He also wrote a comprehensive review on the RED process [60]. Then, Audinos compared the applicabilities of two different types of ED membranes (one pair of homogeneous and one pair of heterogeneous membranes) in RED operations. In addition, they investigated the salt solution (NaCl vs. ZnSO_4) on power output [61]. In the mid-1980s, Jagur-Grodzinski studied the effect of hydrodynamics (different salt solution streams) on RED [62]. At the end of the 20th century and early in the 21st century, despite its promise, the number of papers on RED was very low and publication stopped. However, recently,

owing to the depletion of fossil fuel sources and related factors, RED has received significant attention once again [63-65]. Today, the RED process developed as a hybrid systems with seawater desalination systems [66], PRO [67], and microbial power cells [68].

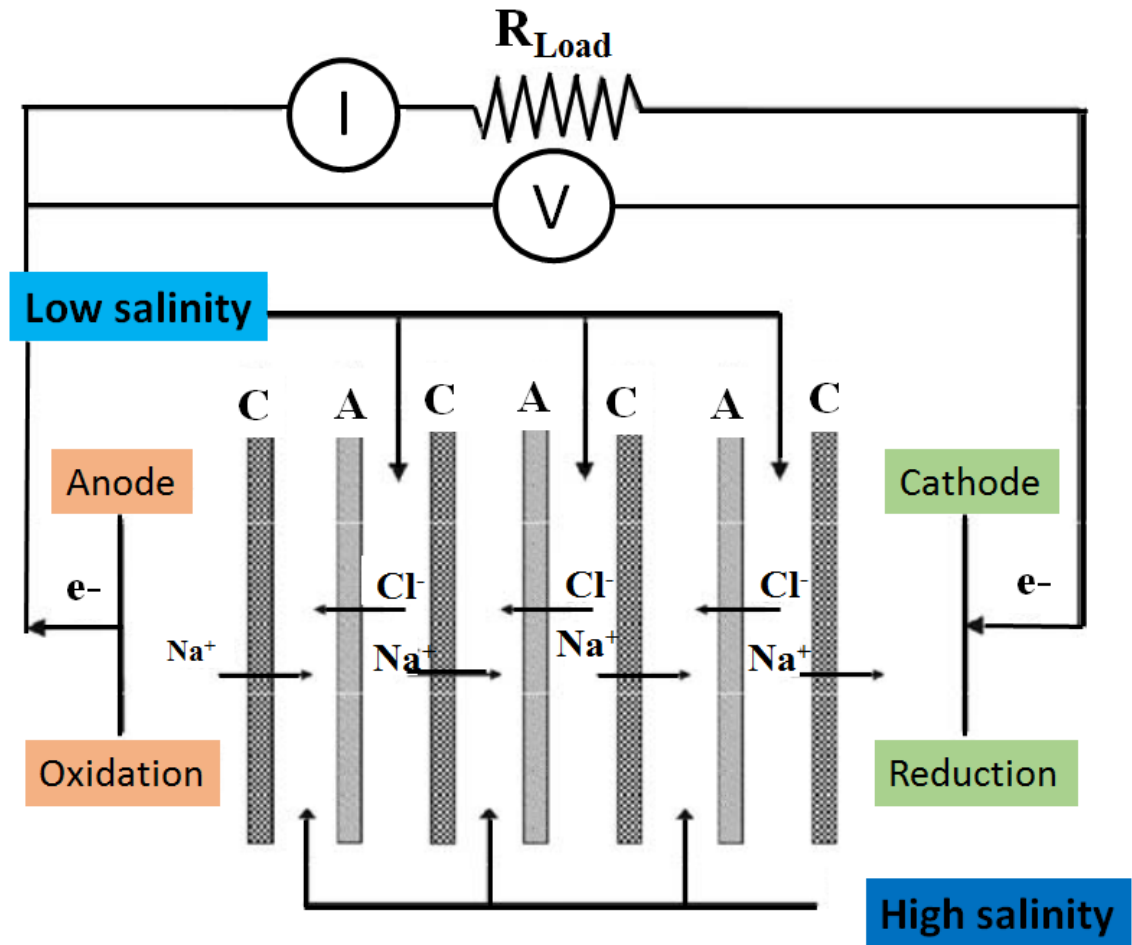


Fig. 1.16 Principle of RED. A is an AEM, C is a CEM, V is the potential difference over the applied external load (V), I is the electrical current (A), and R_{Load} is the resistance of the external load (Ω).

1.4.3. Fouling in RED processes

In an RED system, since seawater is used as high salinity water, biofouling of AEMs is a severe problem [46]. Previous studies have shown that without specific anti-

fouling strategies, the power density will decrease sharply to 60% of the initial power in the first several hours of operation (Fig. 1.17) [69]. This reduction in power density was related to biological fouling. Most of the studies on the improvement of fouling resistance focused on system design (i.e., compartment thickness, type of spacer) or operation conditions (i.e., flow rate, electrical load). He et al. were able to decrease fouling in an RED system by using different types of spacers. They prepared a spacer with a new design that sufficiently improved power density and simultaneously lowered the membrane fouling tendency [70]. Fig. 1.18 shows the effects of two different feeding solutions (new design of spacers and traditional spacers). Field emission SEM (FE-SEM) images showed that the anti-fouling performances of the CEM and AEM under the new feeding pattern system (new design of spacers) were sufficiently improved.

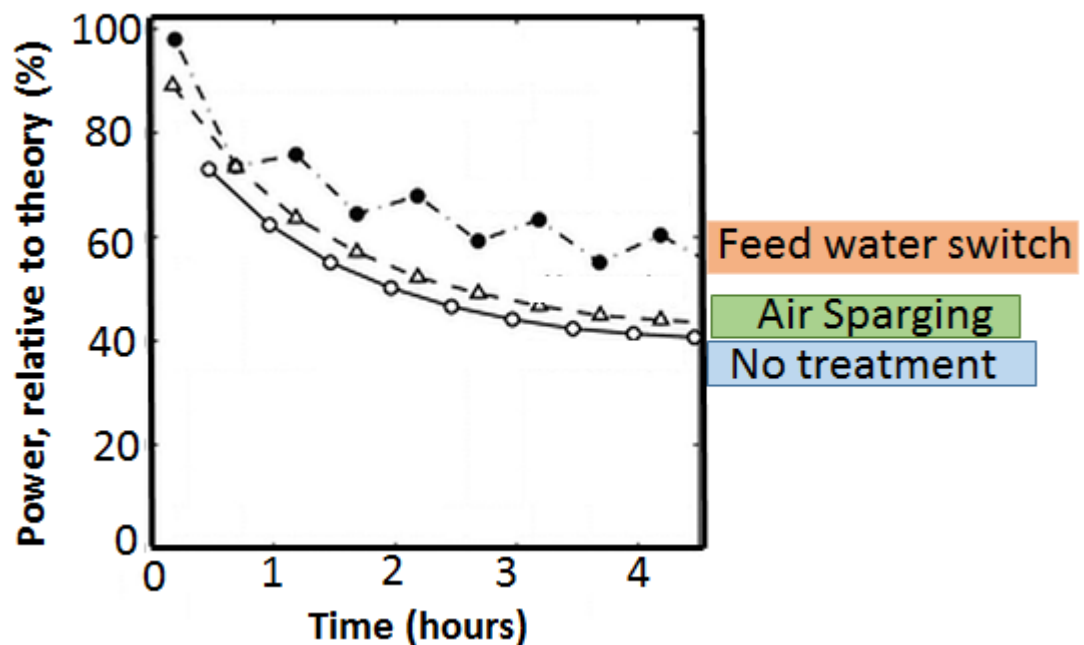


Fig. 1.17 Rapid decrease in power generation in the first several hours [69].

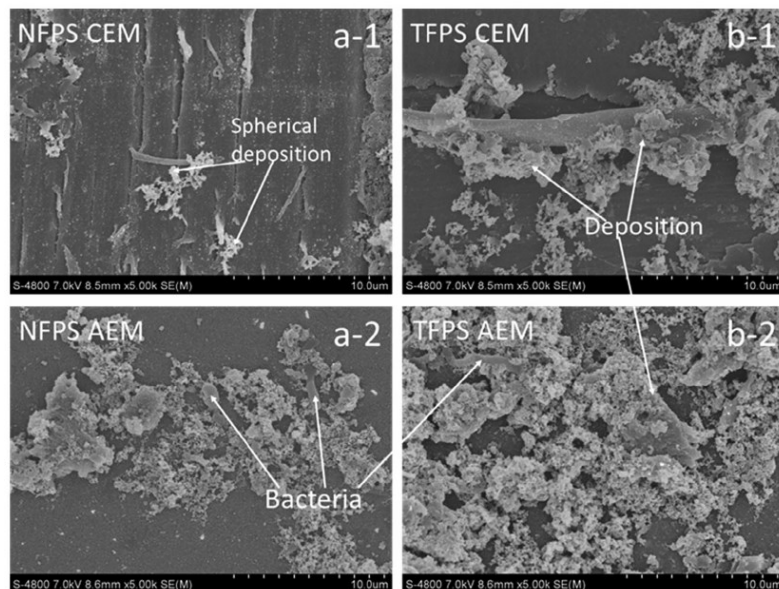


Fig. 1.18 SEM images of the CEM (a-1) and AEM (a-2) under the new feeding pattern system (new spacer design) and the CEM (b-1) and AEM (b-2) under the traditional feeding pattern system (traditional spacer design) [70].

There have been very few attempts to improve anti-fouling properties by modifying the surface of the AEM. In this study, I attempted to improve the anti-fouling properties by surface modification of AMX (chapter 6).

1.5. Aim and scope of this study

As already mentioned, IEMs are applied in a wide range of electromembrane separation processes. Among them, two of the most important processes are ED and RED. ED is utilized for water treatment to address water scarcity and RED is utilized for sustainable energy generation to deal with increasing energy demands and weather pollution due to the use of fossil fuels.

ED is an electrochemical membrane process that uses cation and anion exchange membranes and has been widely applied for the desalination and purification of sea

water, brackish water, and waste water for more than half a century. The most notable advantages of ED are the following:

- High water recovery because of the lack of osmotic pressure limitation
- Excellent membrane durability owing to high mechanical and chemical stability
- Ability to remove harmful monovalent anions such as F^- and NO_3^-
- Ability to remove heavy metals and preparation of softening water

Even though ED has such advantages, improved monovalent anion permselectivity and anti-fouling properties of AEMs in order to enhance ED performance are demanded. Thus, in this study, I attempted to improve the monovalent anion permselectivity and anti-fouling properties of AEMs via surface modification with PDA.

In addition, IEMs are applied in RED processes to extract energy from two water streams with different salt concentrations. In RED processes, seawater is often used as a feed solution for the concentrate compartment. Therefore, biofouling of AEMs in this process is a serious problem. Hence, I investigated the biofouling behavior of AEMs during RED operations and attempted to improve the anti-biofouling properties of AEMs via the same modification method as that used for ED performance enhancement.

Excluding chapter 1 (general information), this thesis can be divided into two main parts:

- The first part (chapters 2 and 3) contains the theoretical and experimental details of the improvement of the monovalent anion permselectivity of AEMs in ED processes.
- The second part (chapters 4–6) describes the improvement of the anti-fouling properties of AEMs in ED and one of its applications (RED).

Here, the chapters of this thesis are introduced in detail:

➤ **Chapter 1:**

In this chapter, general information about membrane technology, its problems, and strategies to deal with issues especially in ED processes were introduced.

➤ **Chapter 2:**

In this chapter, the effects of several parameters of the system (including the AEM) on the anion permselectivity are explained theoretically using a previously proposed equivalent circuit model. In addition, a method to estimate the monovalent anion selectivity from the physicochemical properties of the system is discussed.

➤ **Chapter 3:**

This chapter describes the modification of a commercial AEM, Neosepta AMX (Astom Corp.), with PDA; this was done in order to experimentally verify the theoretical discussion and predictions in chapter 2. The permselectivity of the PDA-modified AEM for NO_3^- , F^- , and SO_4^{2-} relative to that for Cl^- were measured. Ion fluxes were obtained from the time course of the amounts of anions (eq) in the dilute compartment during ED. Anion concentration was measured using an ion chromatograph. In addition, membrane resistance was measured using single-electrolyte solutions (0.5 keq/m^3) of NaCl, NaF, NaNO_3 , and Na_2SO_4 as the electrolyte solutions to determine the permselectivities for the anions.

Furthermore, experimental data were analyzed using a theoretical model and the charge density of the negatively charged layer of the AMX surface was determined.

➤ **Chapter 4:**

This chapter describes the modification of a commercial AEM, Neosepta AMX (Astom Corp.) with PDA, which was done to improve its anti-organic fouling properties. The hydrophilicity and surface charge density were determined by measuring the water contact angle and ζ potential, respectively. The anti-organic fouling potential of AMX was evaluated with respect to transition time, i.e., the amount of time that elapsed before fouling occurred, using SDBS as a model organic foulant. In addition, the fouling data were analyzed theoretically using the previously proposed model. The optimal dopamine concentration and deposition time were determined. Furthermore, the stability of the PDA coating layer was investigated.

➤ **Chapter 5:**

Similar to chapter 4, this chapter describes the modification of Neosepta AMX (Astom Corp.) with PDA to improve its anti-adhesion properties, which improves the anti-biofouling potential of the membrane. The anti-adhesion properties were evaluated using an immersion test with a suspension of *P. putida* bacteria as a biofoulant under ED operation. After immersion test, membrane surfaces were observed using CLSM and analyzed using COMSTAT software; the average amount of total cells, coverage percentage, and average thickness of the biofilm that formed on the membrane surface were calculated. The anti-biofouling performance under ED operation was evaluated by measuring the increase in transmembrane potential due to the increase in the electric resistance of the membrane caused by biofouling. The concentration of the *P. putida* bacteria suspension used as the feed solution was ten times higher than that of the suspension used in the immersion test. Then, for further investigation, fouled

membranes were observed using SEM. The coverage percentage of bacteria was obtained by analyzing the SEM images. In addition, the effect of DC on anti-biofouling performance and bacterial attachment was investigated through the SEM images.

➤ **Chapter 6:**

This chapter describes the evaluation of the anti-biofouling properties of unmodified and PDA-modified AMX membranes under RED operation using *P. putida* bacteria suspension as a biofoulant. Fouled membranes were then examined using SEM. Coverage percentage of bacteria was obtained by analyzing the SEM images. In addition, biofouling under ED and RED operation were compared with that in the immersion test.

➤ **Chapter 7:**

The conclusions of this dissertation are summarized in this chapter.

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Chapter 2

Theoretical study of the permselectivity of an anion exchange membrane in electrodialysis

2.1. Introduction

Recently, water shortage has been a serious problem, globally. Many membrane processes are used to produce drinking water from seawater, underground water and other water sources. Electrodialysis (ED) is one of the useful membrane processes as well as reverse osmosis (RO) and nanofiltration (NF) processes. ED is an electrochemical separation process that uses an ion permselectivity of cation and anion exchange membranes [1]. In ED processes, ions are selectively transported from one compartment (the diluted compartment) to another compartment (the concentrated compartment) through ion exchange membranes (IEMs) under the driving force of an electrochemical potential gradient. One advantage of ED compared with other processes, such as RO, is that a higher brine concentration can be achieved because there are no osmotic pressure limitations. Notably, ED is used to remove harmful ions such as F^- and NO_3^- [2-7]. It can also be used to soften water [8] and to remove heavy metals [9].

One of the most important properties of IEMs is the permselectivity towards specific ions. In particular, the monovalent anion selectivity of anion exchange membrane (AEM) is very important, because most of the harmful anions that should remove from feed water are monovalent, such as F^- and NO_3^- . Infants younger than 6 months old are susceptible to nitrate poisoning because, within an infant's body, nitrate is changed to toxic nitrite by bacteria. Once formed, nitrite enters the blood-stream and forms methemoglobin, which interferes the blood's ability to carry oxygen [10]. High concentration of fluoride in drinking water results in fluorosis (dental/skeletal abnormalities) and several types of neurological damage [11]. In addition, AEMs must be impermeable to sulfate ions to prevent the precipitation of calcium sulfate during the ED process [12]. Calcium sulfate precipitates as a scale in the concentrated compartment, causing serious problems in the ED process. Moreover, by selectively removing target ions from feed solutions, it is possible to produce high quality water to satisfy specific water standards. Thus, high monovalent anion selectivity is demanded for AEMs. A monovalent ion permselective membrane has the capability to separate monovalent ions from a solution containing both mono- and multi-valent ions [13]. It has been reported that the selectivity for sulfate ions (relative to chloride ions) depends on the method used to prepare an AEM in the ED process [14]. It is also known that the permselectivity of specific anions through the AEM depends on the hydration energy of the anions and the hydrophilicity of the membrane, apart from the membranes having a negatively charged layer on the membrane surface [12, 15].

A number of researchers have investigated the fabrication of AEMs with high monovalent anion selectivity [12-14, 16, 17]. However, as far as we know, there have

been few theoretical investigations on the monovalent anion selectivity of ED system. Identifying and understanding the parameters that affect monovalent anion selectivity will allow us to theoretically estimate the monovalent anion selectivity from physicochemical properties of system. This would also provide us a good understanding of fundamental nature of ED and a guideline to fabricate AEMs with high monovalent selectivity. In addition, it would be very useful in the design of ED process.

An equivalent circuit model [6] was proposed by our group to explain the performance of ED process. I showed this model fit very well with experimental results. In this chapter, I theoretically discuss the effect of several parameters of system (including AEM) on the monovalent selectivity using the equivalent circuit model. I then discuss the way to estimate the monovalent selectivity from physicochemical properties of system.

2.2. Theoretical

2.2.1. Equivalent circuit model

Figure 2.1 shows the fundamental system of ED. In ED system, the feed solution is divided by the pair of anion exchange membrane (AEM) and cation exchange membrane (CEM). When a DC voltage is applied to the system, anions migrate towards the anode through the AEM while cations migrate to the cathode through CEM. However, anions cannot permeate the CEM and cations cannot permeate the AEM because of the electric repulsion between ions and membrane charge. Consequently, the ion concentration in the central compartment between AEM and CEM decreases. The central compartment is thus called the “diluted compartment”. At

the same time, the ion concentration increases in the compartment next to the diluted compartment and therefore this compartment is called the “concentrated compartment”.

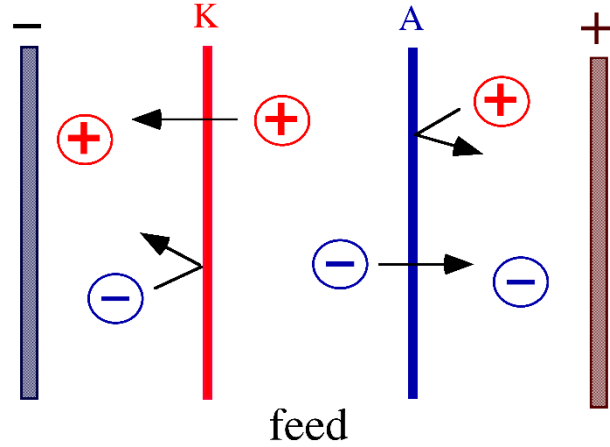


Fig. 1.1 Fundamental system of ED. K: cation exchange membrane (CEM);

Considering k indicates all ionic species including cations and anions, the ion flux of ion k through the membrane, J_k (eq/s m²) is obtained from the electrochemical potential gradient and is given by Eq. (2.1) [18, 19].

$$J_k = -\frac{\alpha_k RT}{N_A} B_k \left(\frac{\partial [k]_M}{\partial x} \right) - z_k \frac{\alpha_k F}{N_A} B_k [k]_M \left(\frac{\partial E_M}{\partial x} \right) \quad (2.1)$$

Here, B_k denotes the diffusion coefficient (m²/sJ) of ion k within the membrane, $[k]_M$ the concentration (eq/m³) of ion k within the membrane and $\partial E_M / \partial x$ the electric potential gradient (V/m) across the membrane. α_k is the parameter that shows the sieving effect of membrane for ion k [20]. z_k denotes the sign of ionic charge of ion k (1 or -1). R denotes the gas constant (J/K eq), T the temperature (K), F the Faraday

constant (C/eq) and N_A the Avogadro constant (1/eq). The first term of right hand side of Eq. (2.1) shows the ion flux due to the diffusion along the concentration gradient and the second term the ion flux induced by the electric potential. The electric potential includes the externally applied potential and the diffusion potential within the membrane. When a membrane divides two electrolyte solutions with different concentration and/or different electrolytes, the potential difference, so called a membrane potential, is generated between two electrolyte solutions. This potential consists of diffusion potential within the membrane and Donnan potentials at membrane/solution interfaces. However, the Donnan potential is a potential resulted from the partition of ions into the membrane and the potential which affects the ion flux is only the diffusion potential [19].

Considering the system which contains n kinds of electrolytes, the concentration of ion partitioned into the membrane is obtained from the electroneutrality condition, Eq. (2.2) and the Donnan equilibrium condition, Eq. (2.3) [21, 22]. In Eq. (2.3), concentration dependency of activity coefficient is neglected and the standard chemical potential within the membrane is assumed to be the same as that in bulk solution.

$$[iI]_M + \dots + [in]_M - [aI]_M - \dots - [an]_M + \theta_M = 0 \quad (2.2)$$

$$\left(\frac{[iI]_M}{[iI]_B} \right)^{1/z_{iI}^v} = \dots = \left(\frac{[in]_M}{[in]_B} \right)^{1/z_{in}^v} = \left(\frac{[aI]_M}{[aI]_B} \right)^{1/z_{aI}^v} = \dots = \left(\frac{[an]_M}{[an]_B} \right)^{1/z_{an}^v} \quad (2.3)$$

where $[in]$ and $[an]$ indicate the concentrations (eq/m³) of cation and anion of n^{th} electrolyte, respectively. z_k^v denotes the ionic valence of ion k . Subscripts M and B indicate the membrane and the bulk solution, respectively. θ_M denotes the membrane charge density (eq/m³) and is assumed to be homogeneous in this study. It is clear from

Eqs. (2.2) and (2.3) that it is impossible to obtain an analytical equation for concentration of each ion partitioned into membrane in general case. Only in some cases, it is possible to obtain the analytical equation.

Here, in this paragraph, I treat the simple system which contains one kind of uni-univalent electrolyte, i^+a^- like NaCl to discuss the fundamental concept. In this case, the concentration of ions partitioned into the membrane are given by Eq. (2.4) from Eqs. (2.2) and (2.3) [19, 21].

$$[i]_M = \{(\vartheta_M^2 + 1)^{1/2} - \vartheta_M\} C_B \quad [a]_M = \{(\vartheta_M^2 + 1)^{1/2} + \vartheta_M\} C_B \quad (2.4)$$

where ϑ_M denotes $\theta_M/2C_B$ and C_B the bulk concentration (eq/m³). In ED system, the membrane charge density of IEM is required to be higher than the bulk concentration, $\vartheta_M \gg 1$, to show a high permselectivity of counterion for membrane charge. The high counterion permselectivity is resulted from the high Donnan exclusion for coion. It is clear from Eq. (2.4) that only counterion is partitioned into IEM and the concentration of coion within the membrane is negligibly small under the condition of $\vartheta_M \gg 1$. In addition, the concentration of counterion within the membrane is equal to the membrane charge density. It means that there is no concentration gradient within the membrane and the diffusion potential is zero under the condition of $\vartheta_M \gg 1$. Thus, it is found from Eq. (2.1) that the ion flux in ED system is determined by the ion flux induced by the externally applied electric potential gradient across the membrane. This discussion will be supported by the report stating that the diffusion contribution is negligible in most of the ED condition [23]. This condition will be satisfied under the condition of $\theta_M > 20C_B$. The membrane charge density is determined from the membrane potential [21, 24] as will

be estimated from the ion exchange capacity (meq/dry-g) of IEM using a specific gravity and a water content.

In ED system, it is well known that the counterion concentration at IEM/bulk solution in diluted compartment interface decreases depending on the electric current density that flows through IEM. This phenomenon is called as a concentration polarization and is caused from the difference of transport number of counterion between in the bulk solution and within the membrane [25, 26]. The current – Voltage curve (I-V curve) shows a plateau over a certain current density called a limiting current density, I_{lim} (A). On the other hand, it is experimentally and theoretically known that the electric current linearly increases with the applied voltage and the I - V curve satisfies the Ohm's law under the condition of $I < I_{lim}$ [26, 27]. Under this condition, the desalinated amount of ion is obtained from the Faraday's law of electrolysis. The limiting current density depends on the bulk electrolyte concentration and is reported as 13.9 mA/cm² for 0.1 M NaCl and 0.7 mA/cm² for 0.005M NaCl [25]. In ED system, electrolytes permeate from the diluted compartment to the concentrated compartment through IEM. Ions partitioned into membrane from the diluted compartment carry the electric current. Thus, the limiting electric current density is determined by the bulk concentration in the diluted compartment.

In this study, I treat the ED system where the membrane charge density is higher than 20 times of the initial feed concentration that is the initial electrolyte concentration of diluted compartment. In other words, I treat the system where the initial feed concentration is lower than $\theta_M/20$. The electric current density that flows through IEM is lower than the half of limiting current density for initial feed

concentration. It is also assumed that all of compartments are effectively stirred to make the electrolyte concentration of compartment homogeneous. In this system, the amount of desalinated ion is obtained by Faraday's law of electrolysis. Hereafter, a constant electric current system is treated.

According to Faraday's law of electrolysis, the amount of desalinated ions is determined by the total amount of current that flows through the system and is given by Eq. (2.5). $Q = I t / F$ (2.5)

where Q (eq) indicates the amount of desalinated ions, I (A) the electric current, t (s) time. Total electric current is the sum of electric current carried by each electrolyte. Then, the equivalent circuit shown in Fig. 2.2 is proposed assuming the system contains n kinds of electrolytes [6]. In Fig. 2.2, R_i^K denotes the electric resistance of the CEM for cation i (Ω), R_a^A the electric resistance of the AEM for anion a (Ω). The total membrane resistance, R^M is given by $R_i^K + R_a^A$. $R_{dilu.}$ denotes the electric resistance of diluted compartment (Ω). Subscript n (figures) denotes n^{th} electrolyte. Each of 1^{st} to n^{th} circuits corresponds to 1^{st} to n^{th} electrolytes, respectively.

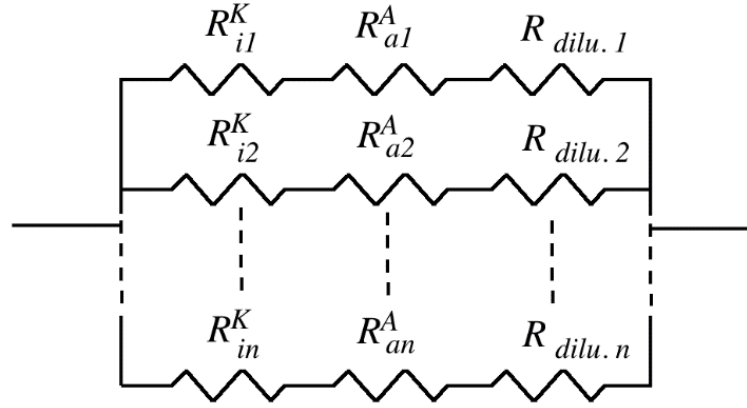


Fig. 2.2 Equivalent circuit of ED. R_{in}^K and R_{an}^A denote the electric resistance of cation and anion exchange membranes for ion transport, respectively. $R_{dilu.n}$ is the electric resistance of the diluted compartment caused by the n th electrolyte.

A practical ED system is generally a continuous processing under constant voltage condition, while I treat a constant electric current system in this study. The practical ED system consists of several cells (pairs of CEM and AEM) and two electrode compartments with electrodes. Thus, the practical ED system consists of several CEMs, AEMs, diluted compartments, concentrated compartments and two electrode compartments with electrodes. The concentrated compartments and electrode compartment also play as an electric resistance. If the system is a constant voltage system, it is needed to take into account these electric resistances to calculate the electric current that flows through the system. Although the practical ED system is a constant voltage system, the dilute stream, concentrate stream and electrode stream flow through the appropriate compartments with respective flow rates and the electric resistances of these compartments are almost constant. Thus, the practical ED system is

also almost constant electric current system. In the constant electric current system, it is not needed to take into account the electric resistances due to concentrated and electrode compartments, since the electric current is always constant everywhere in the system. In addition, even if the system consists of several cells, the total amount of desalinated ions is calculated by (amount of desalinated ions through one cell)×(number of cells). Then, the equivalent circuit model shown in Fig. 2.2 is enough to treat the ED system.

2.2.2. Permselectivity

Permselectivity is generally discussed with a transport number ratio between target ion and standard ion. The chloride ion is commonly treated as a standard ion. Putting am as the target anion and an as the standard anion, the transport number ratio between am and an , P_{an}^{am} is defined by Eq. (2.6) [28]:

$$P_{an}^{am} = (t_{am} / [am]_B) / (t_{an} / [an]_B) = (J_{am} / J_{an}) ([an]_B / [am]_B) \quad (2.6)$$

where t_{am} and t_{an} denote the transport numbers of anions am and an , respectively. $[am]_B$ and $[an]_B$ are the concentrations (eq/m³) of anions am and an in the diluted compartment, respectively. J_{am} and J_{an} denote the fluxes (eq/m²s) of anions am and an , respectively. In Eq. (2.6), the transport number is divided by concentration, because the transport number depends on the concentration, even though P_{an}^{am} is called the transport number ratio. Thus, P_{an}^{am} represents the transport number ratio for unit concentration and is obtained from ion fluxes and concentrations in the diluted compartment.

The amount of desalinated ion is given by Eq. (2.5). Thus, according to Fig. 2.2, the flux of n^{th} electrolyte is obtained from the electric current that flows through the n^{th} circuit. In ED, as I discussed in Section 2.1, the ion flux through the membrane is

mainly determined by the ion flux induced by the externally applied voltage. The voltage applied to cell, E (V) is the common for all circuits from 1st to n^{th} circuit. The electric current, I_n (A) carried by n^{th} electrolyte through n^{th} circuit is given by Eq. (2.7).

$$I_n = F J_n M_s = E / (R_{in}^K + R_{an}^A + R_{dilu,n}) = E / R_n \quad (2.7)$$

where J_n is the flux of n^{th} electrolyte and M_s the membrane surface area (m^2). The summation of Eq. (2.7) over electrolytes, ΣI_n gives a total electric current. From Eq. (2.7), J_n is given by Eq. (2.8) and P_{an}^{am} is rewritten by Eq. (2.9).

$$J_n = E / \{(R_{in}^K + R_{an}^A + R_{dilu,n}) F M_s\} \quad (2.8)$$

$$P_{an}^{am} = \{(R_{in}^K + R_{an}^A + R_{dilu,n}) / (R_{im}^K + R_{am}^A + R_{dilu,m})\} ([an]_B / [am]_B) \quad (2.9)$$

It is clear from Eq. (2.9) that P_{an}^{am} is obtained if the electric resistance of all circuits are known.

In Eq. (2.9), $R_{dilu,n}$, the resistance in the diluted compartment (Ω) due to n^{th} electrolyte, is determined by the equivalent conductivity of n^{th} electrolyte and is given by

$$R_{dilu,n} = \{1/(\lambda_{in}[in]_B + \lambda_{an}[an]_B)\} (l_{dilu}/M_s) = \{1/(\lambda_{in} + \lambda_{an})[ian]_B\} (l_{dilu}/M_s) \quad (2.10)$$

where λ_{in} and λ_{an} denote the equivalent conductivities ($\text{S m}^2/\text{eq}$) of ions in and an respectively. l_{dilu} is the thickness of diluted compartment (m). $[ian]_B$ denotes the concentration (eq/m^3) of n^{th} electrolyte in the diluted compartment. Thus, it is possible to calculate $R_{dilu,n}$, because λ_{in} and λ_{an} are generally known and l_{dilu} is determined by ED system.

The membrane resistance is determined from the ion flux through the membrane. Thus, the flux of ion k through the membrane J_k is given by Eq. (2.11) from Eq. (2.1), since the concentration gradient of ion and the diffusion potential are zero.

$$J_k = -z_k \alpha_k U_k [k]_M \frac{\partial E}{\partial x} \quad (2.11)$$

where z_k denotes the sign of ionic charge of ion k (1 or -1), U_k is FB_k/N_A and the apparent mobility within the membrane (m^2/sV), $[k]_M$ the concentration (eq/m^3) within the membrane and $(\partial E/\partial x)$ the externally applied electric potential gradient across the membrane (V/m). The flux is obtained by integrating Eq. (2.11) over the membrane thickness. The electric current carried by electrolyte is obtained from the flux using Faraday's law. The membrane resistance, R_{in}^K and R_{an}^A are obtained from the electric current using Ohm's law and are given by Eq. (2.12). $R_{in}^K = l_M^K/\alpha_{in}U_{in}FM_s [in]_M$, $R_{an}^A = l_M^A/\alpha_{an}U_{an}FM_s[an]_M$ (2.12)

where l_M^K and l_M^A indicate the membrane thicknesses (m) of CEM and AEM, respectively.

It is found from Eq. (2.12) that the membrane resistance is increased by decreasing the ion concentration within the membrane. The ion concentration in Eqs. (2.11) and (2.12) is the concentration of ion partitioned from the diluted compartment, since ions partitioned from the diluted compartment carry the electric current as I discussed in Section 2.1. The ion concentration in Eq. (2.12) is obtained from Eqs. (2.2) and (2.3). In the case where all electrolytes are uni-univalent electrolytes, the concentrations of ions partitioned into the membrane are given by Eq. (2.13), considering that the membrane charge density is much higher than the total electrolyte concentration in the diluted compartments, C_B which is the sum of concentration of all electrolytes in the diluted compartment [6].

$$[in]_M = \theta_M^K[in]_B/C_B = \theta_M^K[ian]_B/C_B, \quad [an]_M = \theta_M^A[an]_B/C_B = \theta_M^A[ian]_B/C_B \quad (2.13)$$

where θ_M^K and θ_M^A denote the membrane charge densities of the CEM and the AEM, respectively. In this case, Eq. (2.12) is rewritten by Eq. (2.14) inserting Eq. (2.13) into Eq. (2.12).

$$R_{in}^K = C_B l_M^K / \alpha_{in} U_{in} F M_s \theta_M^K [ian]_B, \quad R_{an}^A = C_B l_M^A / \alpha_{an} U_{an} F M_s \theta_M^A [ian]_B \quad (2.14)$$

In any case, it is difficult to theoretically predict the membrane resistance, because it is difficult to theoretically predict the value of $\alpha_i U_i$ and $\alpha_a U_a$. However, the membrane resistance can readily be measured. Once I measure the membrane resistances, it is possible to calculate the transport number ratio, because the electric resistance of the diluted compartment is calculated using equivalent conductivity data. In addition, it is possible to estimate the variation in membrane resistance caused by the variation of electrolyte concentration using Eq. (2.14).

2. 3. Discussion

2. 3.1. Effect of feed concentration and thickness of diluted compartment

In this section, I treat a system that contains two kinds of uni-univalent electrolytes, such as NaCl and NaNO₃ for simplicity. In this system, from Eqs. (2.9), (2.10) and (2.14), the transport number ratio is given by Eq. (2.15) [6].

$$P_{an}^{am} = (a + b C_B) / (c + d C_B) \quad (2.15)$$

where:

$$a = l_{dilu} / (\lambda_{in} + \lambda_{an}) \quad (2.16)$$

$$b = l_M^K / (\alpha_{in} U_{in} F \theta_M^K) + l_M^A / (\alpha_{an} U_{an} F \theta_M^A) \quad (2.17)$$

$$c = l_{dilu} / (\lambda_{im} + \lambda_{am}) \quad (2.18)$$

$$d = l_M^K / (\alpha_{im} U_{im} F \theta_M^K) + l_M^A / (\alpha_{am} U_{am} F \theta_M^A) \quad (2.19)$$

Here, a and c correspond to the electric resistance of diluted compartment for n^{th} and m^{th} electrolytes, respectively. b and d corresponds to the total membrane resistance for n^{th} and m^{th} electrolytes, respectively.

Figure 2.3 shows P_{an}^{am} as a function of C_B for various thickness of diluted compartment, l_{dilu} . In Fig. 2.3, I assumed $(\lambda_{in} + \lambda_{an})$ to be $126 \times 10^{-4} \text{ S m}^2 \text{ eq}^{-1}$ and $121 \times 10^{-4} \text{ S m}^2 \text{ eq}^{-1}$ for $(\lambda_{im} + \lambda_{am})$. These values correspond to the equivalent conductivities of NaCl and NaNO₃, respectively. I also assumed $4 \times 10^{-4} \Omega \text{ m}^2$ for b , because b is the sum of R_{in}^K and R_{an}^A and the electric resistance of IEMs are almost $2 \times 10^{-4} \Omega \text{ m}^2$ for NaCl [29]. In Fig. 2.3(a), b/d is 10 and 0.1 in Fig. 2.3(b). b/d corresponds to R_n^M/R_m^M , the ratio of total membrane resistance between the standard and target ions. In Fig. 2.3(a), I implicitly assume that the valence of counter ion for iam is different from that for ian . If the counter ion is common, the largest value of R_n^M/R_m^M is 2(= $(2+2) \times 10^{-4} / (2+0) \times 10^{-4}$). This indicates as shown by Eq. (2.9) that the membrane resistance of CEM also affects the permselectivity of anions.

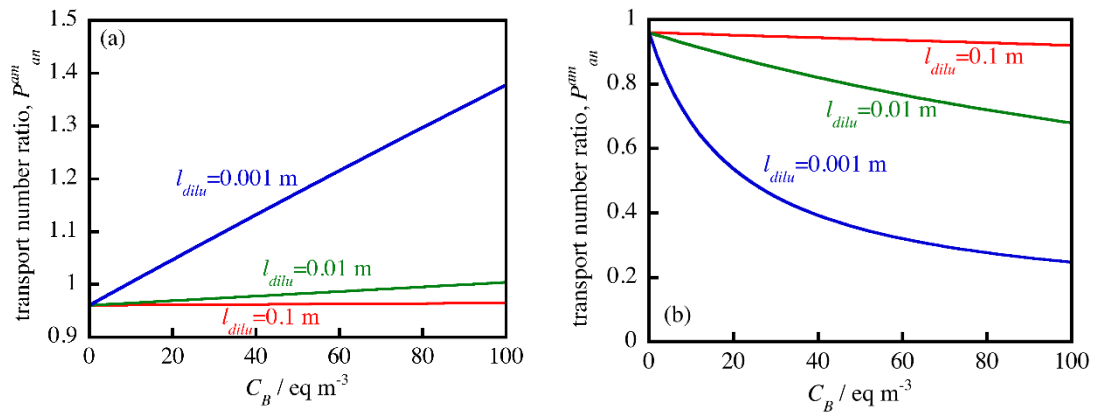


Fig. 2.3 Effect of feed concentration in diluted compartment on P_{an}^{am} for various thickness of diluted compartment. l_{dilu} indicates the thickness of diluted compartment. R_n^M/R_m^M is (a) 10 and (b) 0.1.

In Fig. 2.3, P_{an}^{am} larger than unity means the system is target anion (am) permselective and P_{an}^{am} smaller than unity indicates it is standard anion (an) permselective. It can be seen from Fig. 2.3 that the transport number ratio is 0.96 at $C_B=0$. This value is a/c in Eq. (2.15) and the ratio between the resistance of diluted compartment (Ω) for the n^{th} and m^{th} electrolytes. This is because, in the case where the concentration in the diluted compartment is very low, the electric resistance of diluted compartment becomes much higher than the membrane resistance. Then, from Eq. (2.15), the transport number ratio is given by a/c . On the other hand, the electric resistance of diluted compartment decreases with an increase in electrolyte concentration. The transport number ratio shifts to the value determined by b/d that is 10 in Fig. 2.3(a) and 0.1 in Fig. 2.3(b). This phenomenon has experimentally reported [6].

In addition, it can be seen from Fig. 2.3 that the thickness of diluted compartment also affects the transport number ratio. Figure 2.4 shows the transport number ratio as a function of the thickness of diluted compartment. It is clear from Fig. 2.4 that the thickness of diluted compartment affects the permselectivity of system. This occurs because the resistance of diluted compartment increases with the thickness of diluted compartment even if the electrolyte concentration is constant. Then, the transport number ratio (the permselectivity of system) shifts to a/c with an increase in l_{dilu} and to b/d with a decrease in l_{dilu} . This means that the thickness of diluted compartment is very important factor not only in reducing the total electric resistance of the ED system, but also for properly reflecting the membrane property on the permselectivity.

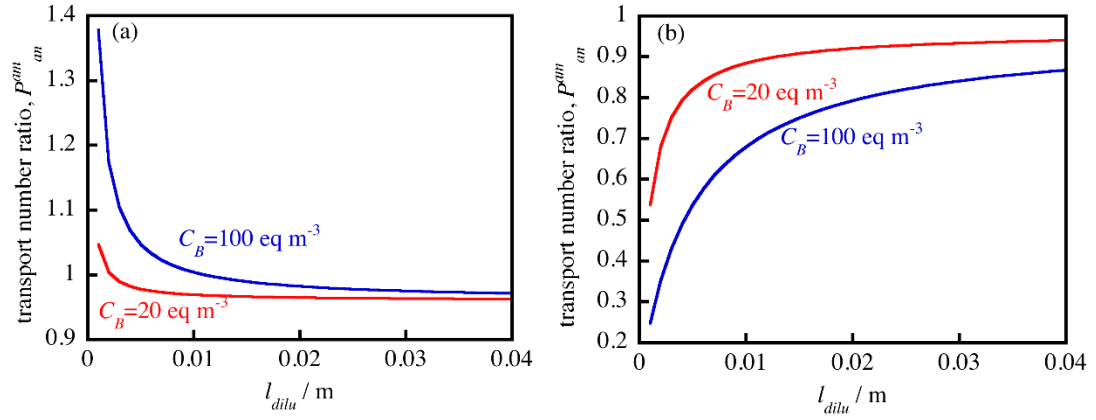


Fig. 2.4 Effect of thickness of diluted compartment on P^{am}_{an} for various feed concentration in diluted compartment. C_B indicates the total electrolyte concentration in the diluted compartment. R^M_n/R^M_m is (a) 10 and (b) 0.1.

2.3.2. Effect of membrane resistance

As shown in Eq. (2.9), the permselectivity is determined by the electric resistances of diluted compartment and membranes. The electric resistance of diluted compartment is determined by the equivalent conductivities of electrolytes and it is not possible to change them. So, the only way to improve the permselectivity is to control the membrane resistances. Thus, in this section, I discuss the membrane resistance.

As I discussed in Section 2.3.1, the transport number ratio (that is permselectivity) is governed the membrane resistance for each anion in the case where the membrane resistance is very high compared with the electric resistance of diluted compartment. It is clear from Eq. (2.12) that the membrane resistance is controlled by the mobility of ions within the membrane and the concentration of ions partitioned into membrane. The mobility of ions within the membrane will be determined by the membrane and ionic species. It will be controlled only by the method of membrane fabrication and this is not

easily controlled. This discussion will be supported by the reports stating that the permselectivity depends on the method used to prepare the AEM [14, 15].

Another way to control the membrane resistance is to control the concentration of ions partitioned into the membrane. The concentration of partitioned ion is controlled by the membrane charge density, because the concentration of partitioned ion is obtained from the electroneutrality condition, Eq. (2.2) and the Donnan equilibrium condition, Eq. (2.3). If the system contains only uni-univalent electrolytes, the amount of partitioned ion is given by Eq. (2.13) and the membrane resistance by Eq. (2.14) assuming the membrane charge density is much higher than feed concentration. In the transport number ratio, Eq. (2.15), the terms related to the membrane resistance are bC_B and dC_B and are given by Eq. (2.20).

$$bC_B = (R_{in}^K + R_{an}^A) [ian]_B = C_B \{ (l_M^K / \alpha_{in} U_{in} F M_s \theta_M^K) + (l_M^A / \alpha_{an} U_{an} F M_s \theta_M^A) \}$$

$$dC_B = (R_{im}^K + R_{am}^A) [iam]_B = C_B \{ (l_M^K / \alpha_{im} U_{im} F M_s \theta_M^K) + (l_M^A / \alpha_{am} U_{am} F M_s \theta_M^A) \}$$

(2.20)

It is found from Eq. (2.20) that the change in membrane charge density does not significantly affect the transport number ratio in the system where all electrolytes are uni-univalent, because the variations in θ_M^K and θ_M^A affect the membrane resistance of ian and iam in the same way. It is impossible to increase (or decrease) only bC_B or dC_B .

On the other hand, in a system which contains monovalent and divalent anions, the amount of ions partitioned into membrane depends on the ionic valence. From Eqs. (2.9), (2.10) and (2.12), through independently controlling the concentrations of an or am partitioned into AEM, the permselectivity can be controlled. Figure 2.5(a) shows the concentration of ions partitioned into the AEM as a function of the positive membrane

charge density numerically calculated with Eqs. (2.2) and (2.3). In Fig. 2.5(a), the system contains two kinds of electrolyte of 10 eq/m^3 . The valence of cation is 1 for both and the valences of anions are -1 and -2 , such as a mixture of NaCl and Na_2SO_4 . If the system contains only one kind of electrolyte, the concentration of anion partitioned into membrane scarcely depends on the ionic valence to satisfy the electroneutrality condition as shown by dotted line in Fig. 2.5(a). Thus, it is clear that the amount of ions partitioned into the membrane is affected by the mixing of anions with different valence. Figure 2.5(b) shows the ratio between divalent anion and monovalent anion concentrations shown in Fig. 2.5(a). It is clear from Figs. 2.5(a) and 2.5(b) that, in mixed solution, the amount of divalent anion partitioned into membrane is higher than that of monovalent anion. The relative concentration of divalent anion compared with monovalent anion increases with increasing membrane charge density. This is because the electrostatic interaction between anion and the positive membrane charge is stronger for divalent anion than for monovalent anion. It means that an AEM commonly has divalent anion selectivity, because the amount of divalent anion partitioned into the membrane is higher than that of monovalent anion and the membrane resistance for divalent anion is lower than that for monovalent anion. Thus, it is clear that the increase in membrane charge density of AEM increases the multivalent anion selectivity and decreases the monovalent anion selectivity.

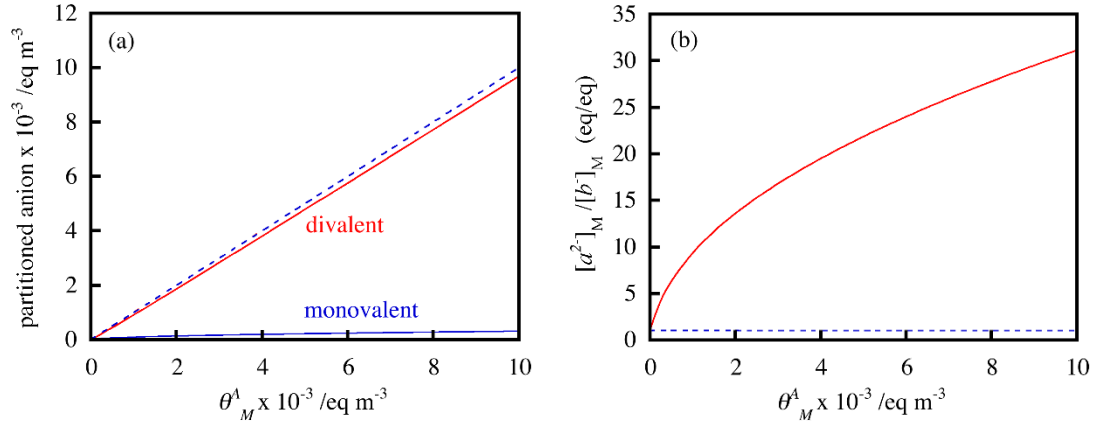


Fig. 2.5 (a) Amount of anions partitioned into membrane and (b) concentration ratio between divalent anion, a^{2-} (eq/m³) and monovalent anion, b^{-} (eq/m³). Dotted lines correspond to single electrolyte solutions and solid lines the mixed solution of two electrolytes, $i^{+}_2a^{2-}$ and $i^{+}b^{-}$. Each concentration is 10 eq/m³. In Fig. 2.5(a), dotted lines for a^{2-} and b^{-} are completely overlapped.

If an increase in positive charge density decreases a monovalent selectivity, an increase of negative charge density at the AEM surface will increase monovalent selectivity. This requires a surface modification of AEM with a negatively charged layer. This concept corresponds to adding membrane resistance caused by the negatively charged layer to each circuit in Fig. 2.2 as shown in Fig. 2.6. This layer acts as an additive resistance, as part of AEM. The negative charge density of this layer, θ^{NL}_M should not be as high as for the CEM, θ^K_M . If θ^{NL}_M is the same order of magnitude as θ^K_M , anions cannot be partitioned into the negatively charged layer and cannot permeate the AEM. Cations are also partitioned into the negatively charged layer to satisfy the electroneutrality condition within the layer, because this layer has a negative charge. However, in ED, only anions can permeate the AEM. Thus, the electric resistance of negatively charged layer is only the resistance for anion, R^{NL}_a just like for the AEM.

R_a^{NL} is given by the same equation as R_{an}^A in Eq. (2.12) putting all parameters related to AEM as parameters related to negatively charged layer.

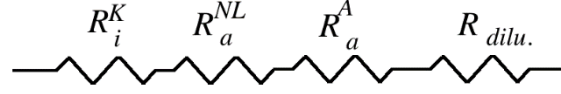


Fig. 2.6 Equivalent circuit with negatively charged layer on AEM. R_a^{NL} indicates the electric resistance of negatively charged layer on AEM surface for anion. $R_a^{NL}+R_a^A$ gives total electric resistance of AEM.

It has already been attempted in practice to modify the AEM surface with a negatively charged layer to improve not only the permselectivity [30] but also an antifouling potential of AEMs [31, 32]. It is possible to obtain this type of AEM commercially [33]. If an effective negatively charged layer can be created on AEM surface, it is expected from Eqs. (2.2) and (2.3) that the amount of divalent anions partitioned into the negatively charged layer would be lower than that of monovalent anions. From Eq. (2.12), this makes the electric resistance for divalent anions higher than that for monvalent anions and increases the monovalent selectivity of AEM. Figure 2.7 shows the amount of ions partitioned into the negatively charged layer as a function of negative charge density. In Fig. 2.7, the electrolyte composition is the same as in Fig. 2.5, two kinds of 10 eq/m³ electrolytes like NaCl and Na₂SO₄. Figure 2.7(a) shows the concentration of anions partitioned into the negatively charged layer and Fig. 2.7(b) the concentration ratio between divalent and monovalent anions shown in Fig. 2.7(a).

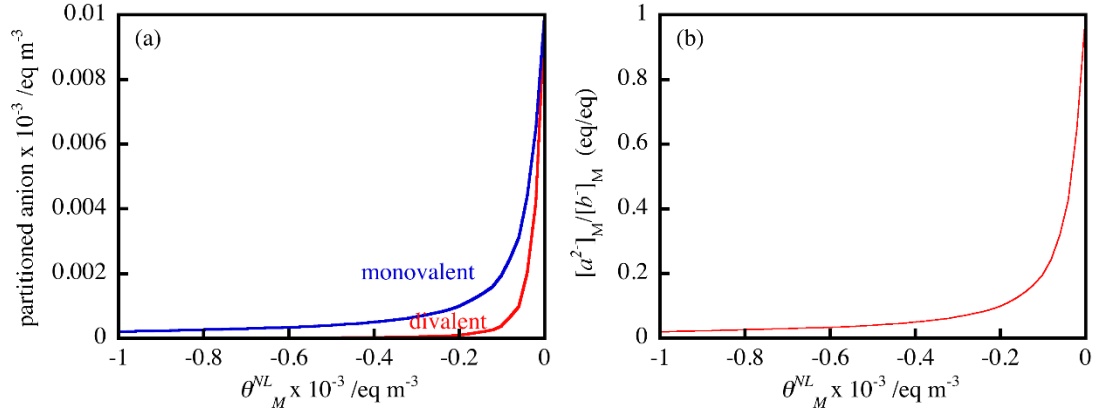


Fig. 2.7 (a) Amount of anions partitioned into the negatively charged layer and (b) the concentration ratio between divalent anion, a^{2-} (eq/m³) and monovalent anion, b^- (eq/m³). The system contains a mixed solution of two electrolytes, $i^+_2a^{2-}$ and i^+b^- . Each concentration is 10 eq/m³. θ_M^{NL} indicates the membrane charge density of negatively charged layer (eq/m³).

It is found from Figs. 2.7(a) and 2.7(b) that the amount of divalent anion partitioned into the negatively charged layer markedly decreases with an increase in negative charge density compared with monovalent anion. Consequently, the concentration ratio between divalent and monovalent anions within the negatively charged layer drastically decreases with the increase of negative charge density. Even if the anion concentration in the negatively charged layer is drastically decreased, it is not expected that the membrane resistance of AEM would drastically increase. Because, the amount of anions partitioned into AEM is determined by the positive membrane charge density of the AEM to satisfy the electroneutrality condition. However, the electric resistance of negatively charged layer for divalent anion will be higher than that for monovalent anion. This means that the total membrane resistance for divalent anion will become higher than that of monovalent anion. Thus, an increase in monovalent anion

selectivity is expected by coating the AEM surface with a negatively charged layer and treating a mixed solution containing monovalent and multivalent anions. If the system contains only uni-univalent electrolytes, an increase in permselectivity for the target ion will not be expected, even if the feed solution is a mixed solution containing several kinds of uni-univalent electrolytes, because the effect of negative charge on partition of anion is the same for every anion in the mixture.

As I discussed above, the monovalent anion selectivity will be increased by coating AEM surface with a negatively charged layer. The resistance of negatively charged layer will be obtained from the difference in membrane resistance between modified and unmodified AEMs. The membrane resistance for each anion will be measured with a single solution, while a mixed solution is used in real ED. In addition, the concentration of electrolyte may be different from that used in ED. Nevertheless, once I obtained the membrane resistances of modified AEM, it will be possible to estimate the membrane resistance for each anion in ED from the variation in concentration of each anion partitioned into the negatively charged layer, because, the resistance of negatively charged layer is inversely proportional to the anion concentration within the negatively charged layer as shown in Eq. (2.12). The concentration of each anion partitioned into negatively charged layer is obtained from Eqs. (2.2) and (2.3). Thus, it will be possible to estimate the monovalent anion selectivity from the membrane resistance measured with single solution. The monovalent anion selectivity in real ED may differ slightly from that predicted using the membrane resistance measured with single solution. However, it will be useful to be

able to estimate the permselectivity from simple experiment such as membrane resistance measurement without requiring an actual ED experiment.

2.4. Conclusion

I theoretically discussed the effect of parameters on the permselectivity of anions using the equivalent circuit model. The results showed that a decrease in thickness of the diluted compartment was very important not only to reduce the electric resistance of system, but also to properly reflect the membrane properties on the permselectivity. It was also shown that the membrane resistance of the CEM also affected the permselectivity of anions of ED system.

The permselectivity of an AEM could be controlled by varying the charge density of AEM in the system that contained a mixed solution of monovalent and multivalent anions. An increase in positive charge density of AEM increased the multivalent anion selectivity, because the concentration of multivalent anion became higher than that of monovalent anion within the AEM. The monovalent anion selectivity could be increased by modifying the AEM surface with a negatively charged layer. This layer acted as an additive electric resistance for the AEM. The amount of multivalent anions partitioned into the negatively charged layer was lower than that of monovalent anions because of Donnan exclusion. Consequently, this phenomenon increased the membrane resistance for multivalent anions and decreased the flux of multivalent anions through the AEM.

According to the equivalent circuit model, the electric resistance of circuit corresponding to each electrolyte is given by the sum of the resistance from the diluted

compartment, $R_{dilu.}$ and the total membrane resistance, $R^M (=R_i^K + R_a^A)$. $R_{dilu.}$ is obtained from the equivalent conductance of corresponding electrolyte. R_{n}^M can be estimated from the membrane resistance measured with a single electrolyte solution. Thus, it is possible to roughly estimate the permselectivity of anions by measuring the membrane resistance for each electrolyte with a single electrolyte solution.

This result is not specific but consistent with general concept. I believe that the theoretical confirmation of the validity of general concept is very important to understand the nature of ED.

[Nomenclature]

B_k : diffusion coefficient of ion k within the membrane (m^2/sJ)

C_B : total electrolyte concentration of diluted compartment (eq/m^3)

E : externally applied voltage (V)

EM : $E +$ diffusion potential within the membrane (V)

F : Faraday constant (C/eq)

I : electric current (A)

I_n : electric current carried by n^{th} electrolyte through n^{th} circuit (A)

ian : n^{th} electrolyte

in, an : cation and anion of ian , respectively

$[in], [an], [ian], [k]$: concentration of in, an, ian and k , respectively (eq/m^3)

J_n : flux of n^{th} electrolyte (eq/m^2s)

J_{am}, J_{an} : flux of am and an , respectively (eq/m^2s)

k : all ionic species including cation and anion

$l_{dilu.}$: thickness of diluted compartment (m)

M_s : membrane surface area (m^2)

N_A : Avogadro constant (1/eq)

P_{an}^{am} : transport number ratio between am and an defined by Eq.(6)

Q : the amount of desalinated ions (eq)

R : gas constant (J/Keq)

R^K_i : electric resistance of CEM for cation i (Ω)

RA_a : electric resistance of AEM for anion a (Ω)

R^M : total membrane resistance, $R^K_i + R^A_a$ (Ω)

R_{dilu} : electric resistance of diluted compartment (Ω)

T : temperature (K)

t : time (s)

t_{am}, t_{an} : transport number of am and an , respectively

U_k : apparent mobility within the membrane, FB_k/N_A (m^2/sV)

z_k, z^v_k : sign of ionic charge (1 or -1) and ionic valence of ion k , respectively

Greek

α_k : sieving effect of the membrane for ion k

θ_M : membrane charge density (eq/ m^3)

$\theta^K_M, \theta^A_M, \theta^{NL}_M$: θ_M of CEM, AEM and negatively charged layer on AEM surface, respectively

$\lambda_{in}, \lambda_{an}$: equivalent conductivity of in and an , respectively ($S\ m^2/eq$)

Subscript

n, m : n^{th} and m^{th} electrolyte, respectively

M, B : membrane and bulk solution, respectively

Abbreviation

AEM: anion exchange membrane

CEM: cation exchange membrane

ED: electrodialysis

IEM: ion exchange membrane

NF: nanofiltration

RO: reverse osmosis

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Chapter 3

Surface modification of an anion exchange membrane to improve the selectivity for monovalent anions in electrodialysis – experimental verification of theoretical predictions

3.1. Introduction

Water is vital for the survival of living matter and it is the backbone of the worldwide economy, because water is essential for most industrial, agricultural, and energy-production activities. However, natural water sources are decreasing and they are being polluted, while the global population is increasing. Nowadays, drinking-water scarcity is a serious problem in the world. Membrane processes such as nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) are used to produce drinking water from seawater, wastewater, and brackish water.

Among these membrane processes, only ED is an electrochemical separation process that uses the ion permselectivity of a cation exchange membrane (CEM) and an anion exchange membrane (AEM). Since Juda and McRae developed a stable, highly selective ion exchange membrane of low electric resistance in 1950 [1], ion exchange

membranes have evolved from a laboratory tool into industrial products with significant technical and commercial impact [2]. ED is one of several useful methods to provide potable water from brackish water and groundwater. ED is generally more economical than reverse osmosis (RO) when the water salinity is less than 5 g/L [3]. One of the advantages of ED over RO is that ED has a higher water recovery [4]. It has been reported that the nominal initial brackish water recovery in an electrodialysis reversal (EDR) system is 80%–90%, while it is 65%–75% in an RO system [5]. This is because there are no osmotic-pressure limitations on the ED process.

In ED processes, ions are selectively transported from one compartment (the diluted compartment) to another compartment (the concentrated compartment) through ion exchange membranes (IEMs) under the driving force of an electrochemical potential gradient. The main driving force for the ED process is the externally applied electric potential gradient across the membrane [6, 7]. ED is used to eliminate heavy metals [8] and to soften water [9]. However, notably, the ED process is used to remove harmful ions such as NO_3^- and F^- [10-13] from feed water. High levels of nitrate in drinking water cause nitrate poisoning in human beings, especially in infants younger than six months. Nitrate (NO_3^-) is changed into toxic nitrite (NO_2^-) by bacteria within the body; nitrite causes the blue-baby syndrome [14]. Thus, according to the World Health Organization (WHO), the nitrate and nitrite levels in drinking water are regulated to be less than $5 \times 10^{-2} \text{ kg/m}^3$ and $3 \times 10^{-3} \text{ kg/m}^3$, respectively [15]. In addition, drinking high-fluoride potable water for a prolonged period can cause fluorosis (skeletal and dental abnormalities) [16] and some neurological diseases [17]. It has been reported that

fluoride in drinking water reduces children's IQ [18]. According to the WHO, the upper limit of the concentration of fluoride in drinking water is 1.5×10^{-3} kg/m³ [15].

The harmful ions that should remove from the feed water are monovalent anions. However, when these ions are removed from the feed water in the ED process, multivalent anions such as SO_4^{2-} are also simultaneously removed. It is not desirable to remove too much of the SO_4^{2-} to prevent the formation of CaSO_4 scale in the concentrated compartment. Precipitation of CaSO_4 scale in the concentrated compartment decreases the performance of the ED process. Therefore, a high selectivity for monovalent (relative to multivalent) anions is required for the ED process to make good quality water that meets drinking water standards. It is known that the permselectivity of the AEM for a specific anion depends on the hydration energy of the anion and on the hydrophilicity of the membrane [19,20]. Yamane et al. have reported that the selectivity for sulfate ions depends on how the membrane was fabricated [21]. Several researchers have investigated the fabrication of AEMs with high selectivity for monovalent anions [19, 21-27].

However, as far as we know, there have been few theoretical investigations on the selectivity of the ED system for monovalent anions. In chapter 2, I theoretically analyzed the effect of several parameters of the system (including the AEM) on the selectivity for monovalent anions in order to identify and understand the parameters that affect the selectivity for monovalent anions [6]. I theoretically predicted the following three points.

1. The selectivity for monovalent anions will be improved by modifying the AEM surface with a negatively charged layer.

2. This surface modification will not affect the selectivity between monovalent anions.

3. It will be possible to roughly estimate the permselectivity for anions by measuring the membrane resistance for each electrolyte with a single-electrolyte solution.

In this chapter, I attempted to experimentally evaluate these theoretical predictions by modifying the AEM surface with polydopamine (PDA). The surface modification with PDA forms a negatively charged layer on the AEM surface. In addition, I obtained the charge density of the negatively charged layer (PDA layer) on the modified AEM by analyzing the permselectivity data.

3.2. Experimental

3.2.1. Materials

A NEOSEPTA AMX membrane (Astom Corp., Tokyo, Japan), which has strongly basic anion exchange groups, was used as the AEM. AMX is a common AEM, and it does not have a remarkable selectivity for monovalent anions. The characteristic properties of AMX are as follows: electric resistance = $(2.0\text{--}3.5) \times 10^{-4} \Omega \text{ m}^2$ and ion-exchange capacity (IEC) = 1.4–1.7 eq/kg of dry membrane [2]. A NEOSEPTA CMX membrane (Astom Corp.) was used as the cation-exchange membrane (CEM). The characteristic properties of CMX are as follows: electric resistance = $(2.0\text{--}3.5) \times 10^{-4} \Omega \text{ m}^2$ and IEC = 1.5–1.8 eq/kg of dry membrane [2].

Dopamine hydrochloride (Sigma-Aldrich, Tokyo, Japan) was used to modify the AMX surface. NaCl, NaF, NaNO₃, and Na₂SO₄ (Wako Pure Chemical Industries, Ltd.,

Osaka, Japan) were used as the electrolytes. All chemicals were used as received. Milli-Q water (Millipore, Bedford, MA, USA) was used in all experiments.

3.2.2. Membrane modification

Polydopamine (PDA) was used to modify the AEM. The dopamine solution used for the modification of the surface was prepared by dissolving a desired amount of dopamine in 15 mM Tris-HCl buffer (pH 8.8). A freshly prepared dopamine solution is clear. However, it begins to change color immediately from transparent to darkish brown upon contact with oxygen in the air, indicating the formation of PDA. PDA is spontaneously formed in an aerobic and alkaline dopamine aqueous solution, as shown in Fig. 3.1. As seen in Fig. 3.1, PDA is an amphoteric substance. The isoelectric point of PDA is reported to be around pH 4 [29, 30]. The PDA layer has a negative charge in the ED process for producing drinking water, since the optimum pH of drinking water is usually 6.5–8.5 [15]. In addition, PDA is a bio-inspired polymer (i.e., bioglue) that deposits nonselectively from solution onto virtually any solid surface [31] and is hydrophilic [32].

The AMX membrane was immersed vertically in the freshly prepared dopamine solution (in contact with atmospheric oxygen) at 30 °C for 24 h. The immersion time was determined from the time course of contact angle of modified AMX surface. The contact angle became almost constant after 24 h immersion (chap. 4). The concentration of dopamine was varied (0.1–1.5 kg/m³) for the experiments. After immersion for 24 h, the membrane was taken out of the dopamine solution and rinsed thoroughly with Milli-Q water for one day. The modified membranes were kept in Milli-Q water until they were used.

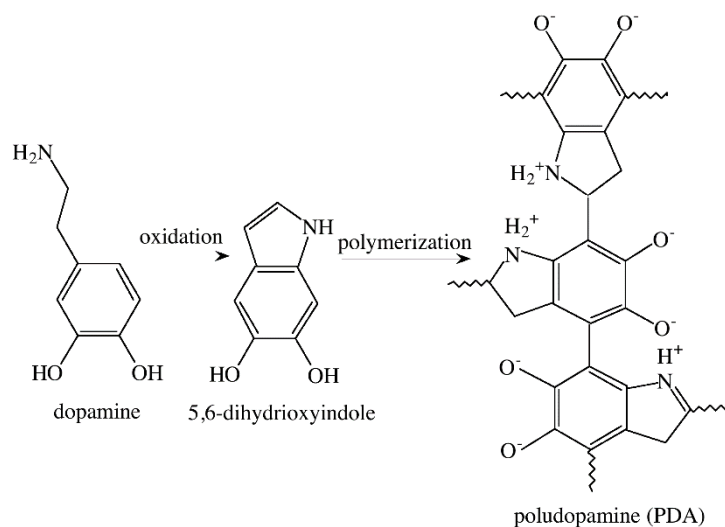


Fig. 3.1. Formation of polydopamine [31,32].

3.2.3. ζ -potential of the modified AMX membrane

The ζ -potential of the modified membrane surface was measured to evaluate the membrane surface charge. The ζ -potential was obtained from the streaming potential measurement by an ELS-4000K instrument (Otsuka Electronics, Osaka, Japan) using 0.01 kg/m³ NaCl solution (pH 6.2) at room temperature. The ζ -potential measurement was repeated at least three times for each sample and mean values were obtained.

3.2.4. Electric resistance of the membrane

It is found from Eq. (2.9) that the electric resistances of the membranes determine the transport number ratio. In order to measure the electric resistance of the AEM, the AEM (effective membrane surface area = $4 \times 10^{-4} \text{ m}^2$ ($0.02 \times 0.02 \text{ m}$)) was clamped tightly between two cells with an Ag/AgCl electrode (cell volume = $1 \times 10^{-4} \text{ m}^3$). The cells were filled with electrolyte solution. The cell resistance was measured at 1 kHz with a Wheatstone bridge apparatus (Yokogawa Hewlett-Packard, Tokyo, Japan) at room temperature. The electric resistance of the AEM was obtained from the difference between the cell resistances with and without membrane. In this experiment, single-electrolyte solutions (0.5 keq/m^3) of NaCl, NaF, NaNO_3 , and Na_2SO_4 were used as the electrolyte solutions to evaluate the effect of the anion. The pH values of the solutions were not adjusted; they were about 6. The electric resistance of the CEM was obtained from the literature [2], since Na^+ is the only cation in our experiment.

3.2.5. Selectivity for monovalent anions

To evaluate the selectivity for monovalent anions in the ED process, the transport number ratio between target anions (F^- , NO_3^- , and SO_4^{2-}) and a standard anion (Cl^-) was measured. In this experiment, the transport number ratio of Eq. (2.6) is rewritten as Eq. (3.1).

$$P_{\text{Cl}}^a = (J_a/[a]_B)/(J_{\text{Cl}}/[\text{Cl}]_B) \quad (3.1)$$

Here, J_a and $[a]_B$ indicate the ion flux of the target anion and its concentration in the diluted compartment, respectively. J_{Cl} and $[\text{Cl}]_B$ indicate the ion flux of Cl^- and its concentration in the diluted compartment, respectively. Ion fluxes were obtained from the time course of the amounts of anions (eq) in the diluted compartment during ED.

Fig. 3.2 shows the experimental setup for ED. In this setup, cell 2 corresponds to the diluted compartment and cell 3 corresponds to the concentrated compartment. Cells 1 and 4 are the electrode compartments. In the electrode compartments, Ag/AgCl electrodes are used to avoid the pH change of solutions due to electrolysis. The AEM was clamped between cells 2 and 3. The CEMs were clamped between cells 1 and 2 and between cells 3 and 4. The effective membrane surface area was $4 \times 10^{-4} \text{ m}^2$ ($0.02 \text{ m} \times 0.02 \text{ m}$) and the volume of each compartment was $1 \times 10^{-4} \text{ m}^3$. The feed solution was agitated thoroughly with a magnetic stirrer, both in the diluted and concentrated compartments. The electrolyte solution was circulated from the reservoir through both compartments at a flow rate of $1.2 \times 10^{-3} \text{ m}^3/\text{min}$. The same solution was used as the electrolyte solution. The direct-current density was kept constant at 20 A/m^2 (a total current of 8 mA) and the temperature was $(30 \pm 1) ^\circ\text{C}$. Every 30 min, 1 mL of the solution was taken from the diluted compartment and the concentrations of the anions were analyzed using an ion chromatograph (Ion Analyzer IA-300, DKK-TOA Corp., Tokyo, Japan). As a result, the volume of diluted compartment is decreased with sampling, while the volume of concentrated compartment is constant. But, the mass flow due to the difference in the volume between the diluted and the concentrated compartments maybe negligibly small. Then, it will not affect the experimental result.

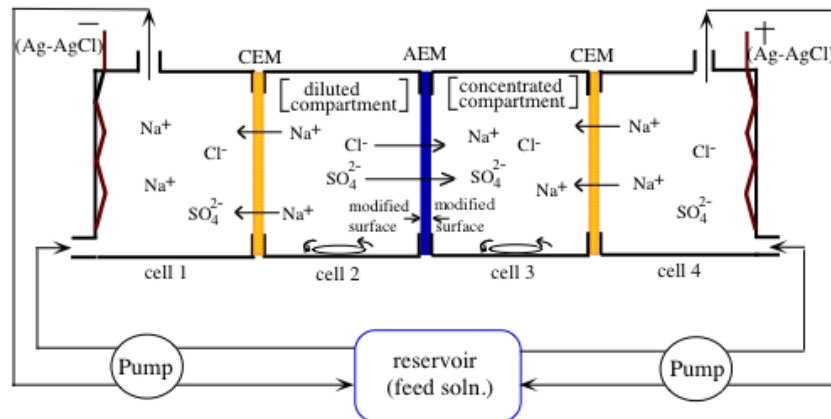


Fig. 3.2. Experimental ED setup to evaluate the anion selectivity of the process. AEM indicates anion exchange membrane and CEM indicates cation exchange membrane. In this figure, the feed solution consists of NaCl and Na₂SO₄.

3.3. Results and discussion

3.3. 1. ζ -potential of the modified AMX membrane

Figures 3.3 shows the ζ -potential of modified AMX membranes as a function of dopamine concentration of dopamine solution. It is found from Fig. 3.3 that the absolute value of negative ζ -potential increased (negative charge density increased) with dopamine concentration, and became constant above 0.5 kg/m³. The increase in negative ζ -potential indicates an increase in electrostatic repulsion between anion and the membrane surface charge, which indicates an improved mono-valent anion selectivity.

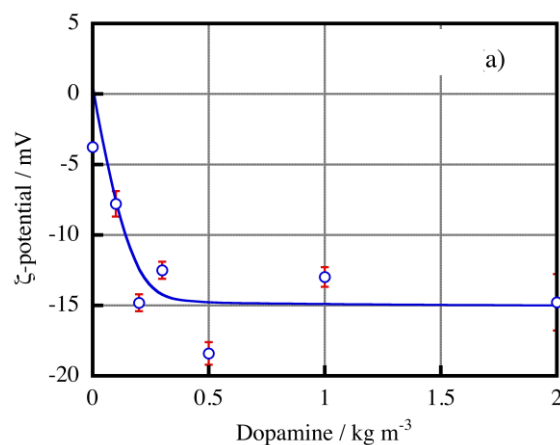


Fig. 3.3. ζ -potential of modified AMX membrane as a function of dopamine concentration. The membranes were immersed in the freshly prepared dopamine solution at 30 °C for 24 h.

3.3.2. Electric resistance of AMX

Fig. 3.4 (a) shows the resistance of PDA-modified AMXs for various anions as a function of the concentration of dopamine of the dopamine solution. In Fig. 3.4 (a), the dopamine concentration of 0 kg/m³ corresponds to unmodified AMX. Fig. 3.4 (b) shows the electric resistance of the PDA layer, obtained from the difference in the electric resistance between unmodified and PDA-modified AMX. It is found from Fig. 3.4 (b) that the resistance of the PDA layer for SO_4^{2-} is significantly higher than those for monovalent anions. This is because the PDA layer has a negative charge under the experimental conditions, since the isoelectric point of PDA is around pH 4 and the pH of the solution used in this experiment was about 6. Thus, the Donnan exclusion of SO_4^{2-} is stronger than those of monovalent anions and the concentration of SO_4^{2-} partitioned into the PDA layer is lower than those of monovalent anions. The electric resistance of the PDA layer for SO_4^{2-} is higher than those for monovalent anions. This indicates that the flux of SO_4^{2-} through the PDA layer will be lower than those of

monovalent anions. Therefore, an improvement of the selectivity for monovalent anions would be expected upon the modification of the surface of AMX with PDA.

In addition, Fig. 3.4 (b) also shows that the electric resistance of the PDA layer monotonically increases with the concentration of dopamine. Because the thickness of the PDA layer increases with the concentration of dopamine. For PDA deposited on rectangular silicon wafers, it has been reported that the thickness of the PDA layer monotonically increases with the concentration of dopamine over a wide range of dopamine concentrations (0-5 kg/m³) [35]. They showed the maximum PDA layer thickness increased from 0 to about 94 nm depending the dopamine concentration. However, a small plateau was reported for dopamine concentrations between 1 and 2 kg/m³. The maximum layer thickness at concentrations of 1–2 kg/m³ was reported to be about 40 nm. The plateau region between concentrations of 1 and 1.5 kg/m³ in Fig. 3.4 corresponds to this phenomenon. Thus, the increase in the electric resistance of the PDA layer in Fig. 3.4 (b) is due to the increase of the PDA thickness layer.

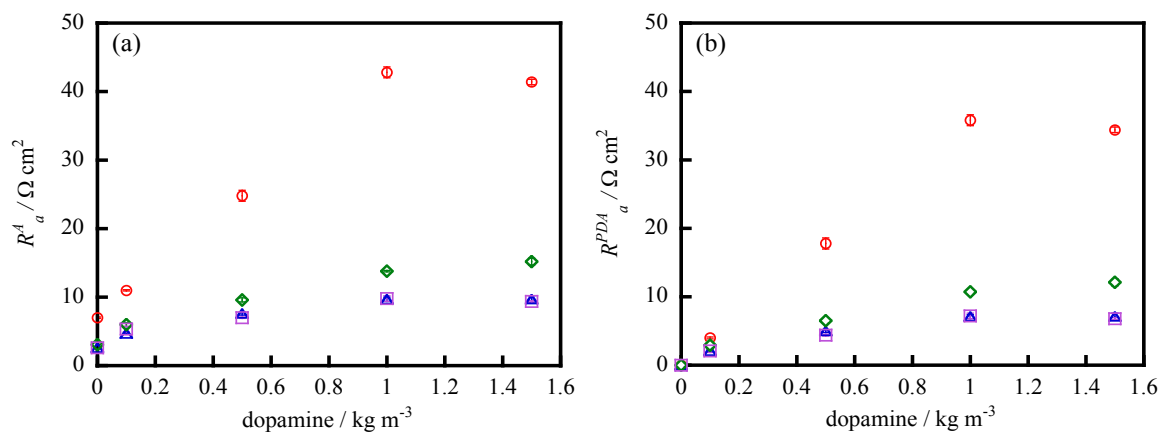


Fig. 3.4. Electric resistance of (a) PDA modified AMXs and (b) the PDA layer for various anions as a function of the concentration of dopamine. Single-electrolyte solutions of sodium salts (0.5 keq/m³) were used in this experiment. $\square$: Cl⁻; $\diamond$: F⁻; $\triangle$: NO₃⁻; $\circ$: SO₄²⁻.

3.3.3. Selectivity for monovalent anions

The transport number ratios of F^- , NO_3^- , and SO_4^{2-} (relative to Cl^-) were measured to investigate the permselectivity of the unmodified and PDA-modified AMXs. The transport number ratio was calculated by substituting the ion flux and ion concentration in the diluted compartment into Eq. (3.1). Fig. 3.5 shows an example of the time course of the amounts of anions in the diluted compartment. Fig. 3.5 (a) shows the data obtained with unmodified AMX and Fig. 3.5 (b) shows the data obtained with PDA-modified AMX. The ion fluxes at time zero (just after the beginning of ED) were obtained from the gradients of the lines shown in Figs. 3.5 (a) and 3.5 (b). Fig. 3.5 (a) shows that the unmodified AMX is selective for divalent anions, since the deionization rates are in the order $SO_4^{2-} > NO_3^- > Cl^- > F^-$. On the other hand, the SO_4^{2-} deionization rate in Fig. 3.9 (b) is lower than the NO_3^- , Cl^- , and F^- deionization rates, which indicates that the PDA-modified AMX is selective for monovalent anions, as I had expected.

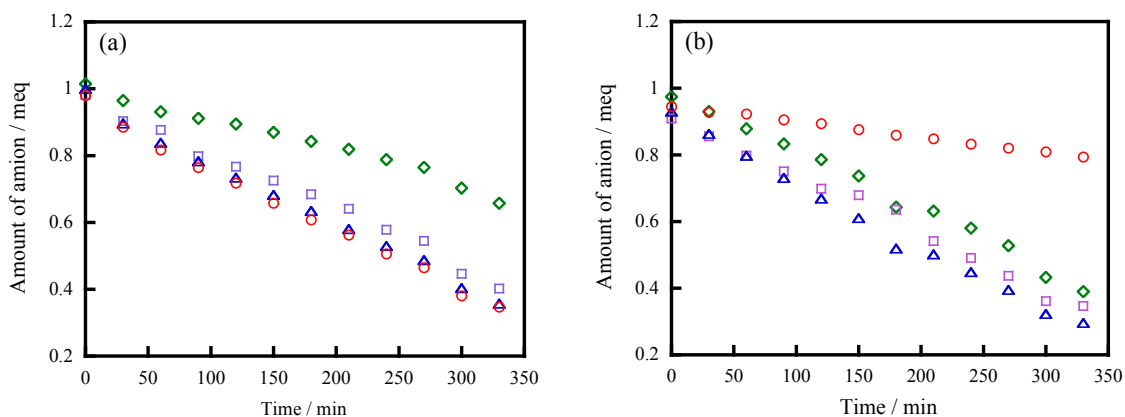


Fig. 3.5. Time course of the amounts of anions (eq) in the diluted compartment for (a) unmodified AMX and (b) PDA-modified AMX membrane (modified with a concentration of dopamine of 1.0 kg/m^3). The electrolyte solution is a mixture of NaCl, NaF, $NaNO_3$, and Na_2SO_4 , with an initial concentration of 0.01 keq/m^3 of each electrolyte. $\square$: Cl^- ; $\diamond$: F^- ; $\triangle$: NO_3^- ; $\circ$: SO_4^{2-} .

Fig. 3.6 shows the transport number ratios of target anions (SO_4^{2-} , F^- , and NO_3^-) relative to a standard anion (Cl^-) as a function of the concentration of dopamine. In the experiment of Fig. 3.6, the feed solution is a mixture of NaCl, NaF, NaNO_3 , and Na_2SO_4 , with an initial concentration of 0.01 keq/m^3 of each electrolyte. In Fig. 3.6, the error bars show the probable errors. However, considering the uncertainties associated with obtaining the gradients of the curves in Fig. 3.5, the value of each data point may have an error of up to ± 0.1 . Fig. 3.6 shows that the transport number ratio between SO_4^{2-} and Cl^- ($P_{\text{Cl}}^{\text{SO}_4}$) is about 1.2 for unmodified AMX (data obtained at a concentration of dopamine of 0 kg/m^3), which reveals that the unmodified AMX is selective for divalent anions. $P_{\text{Cl}}^{\text{SO}_4}$ decreases to ca. 0.22 with an increase in the concentration of dopamine, which indicates that the selectivity of AMX for monovalent anions significantly improves by the modification with PDA, as theoretically predicted. It means the monovalent anion selectivity of PDA modified AMX is higher than the commercial AEM.

On the other hand, the transport number ratios of NO_3^- and F^- relative to Cl^- (i.e., $P_{\text{Cl}}^{\text{NO}_3}$ and P_{Cl}^{F}) do not change so much upon modification with PDA; they remain almost constant (around 1.1 and 0.8, respectively), as theoretically predicted. This is because the Donnan exclusion (by the PDA layer) of SO_4^{2-} is higher than that of monovalent anions. In addition, the Donnan exclusion is determined by the ionic valence. The Donnan exclusion of monovalent anions does not depend on the ionic species and is the same for all monovalent anions. The difference between $P_{\text{Cl}}^{\text{NO}_3}$ and P_{Cl}^{F} is attributed to the difference in Gibbs hydration energy of these anions [19]. The

Gibbs energies of hydration ($-\Delta G_h^\circ$) of F^- , Cl^- , and NO_3^- are 434, 317, and 270 kJ/mol, respectively [19]. The anion with the lowest Gibbs energy of hydration (i.e., NO_3^-) is most easily dehydrated and permeates through AMX more easily than F^- .

It is clear from Fig. 3.6 that the first two of our theoretical predictions, described in Section 3.1, are confirmed experimentally.

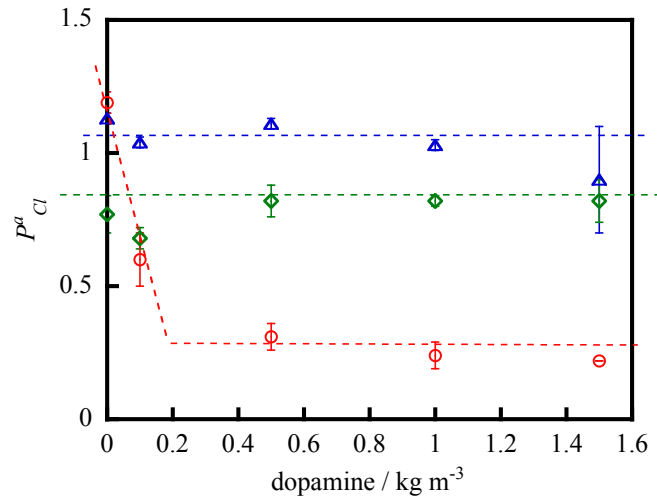


Fig. 3.10. Transport number ratios between target anions (SO_4^{2-} , F^- , and NO_3^-) and Cl^- (P^a_{Cl}) as a function of the concentration of dopamine. In this figure, the feed solution is a mixture of NaCl, NaNO₃, NaF, and Na₂SO₄, in which the initial concentration of each electrolyte is 0.01 keq/m³. Symbols show the experimental data and lines are smoothed lines. Δ : $P^{NO_3}_{Cl}$; $\diamond$: P^F_{Cl} ; $\circ$: $P^{SO_4}_{Cl}$.

Fig. 3.7 shows $P^{SO_4}_{Cl}$ measured for a mixture of 0.25 keq/m³ NaCl and 0.25 keq/m³ Na₂SO₄. In this experiment, the total ion concentration (0.5 keq/m³) is the same as that used to measure the electric resistance of AMX. In Fig. 3.7, the solid line shows the values calculated with Eq. (2.9). In Eq. (2.9), an corresponds to Cl^- and am to SO_4^{2-} . In this calculation, electric resistances that correspond to 0.5 keq/m³ single-electrolyte solutions were used. The resistances of AMX for Cl^- and SO_4^{2-} were obtained from Fig.

3.4 (a). The resistance of CMX was obtained from the literature and is $2 \Omega \text{ cm}^2$ [2]. In our experiment, the effective surface area was 4 cm^2 ; therefore, 0.5Ω was used as the resistance of CMX. The resistance of the diluted compartment was calculated with the equivalent conductivity of each ion. The equivalent conductivities of Na^+ , F^- , NO_3^- , Cl^- , and SO_4^{2-} are 50.11×10^{-4} , 55×10^{-4} , 71×10^{-4} , 76×10^{-4} , and $80 \times 10^{-4} \text{ S m}^2/\text{eq}$, respectively [34]. Table 3.1 shows the values of the resistances used in this calculation. It is clear from Fig. 3.7 that the estimated values (solid line) from the data for single-electrolyte solutions fit the experimental results. Thus, our third theoretical prediction, described in Section 3.1, is confirmed experimentally.

In Fig. 3.7, the solid line fits the experimental data for the solution containing a mixture of $0.25 \text{ keq/m}^3 \text{ NaCl}$ and $0.25 \text{ keq/m}^3 \text{ Na}_2\text{SO}_4$. However, this line is completely different from the line for $P^{SO_4}_{Cl}$ shown in Fig. 3.6. Because the concentration of each ion in Fig. 3.6 is 0.01 keq/m^3 , which is extremely different from the concentration used to calculate the solid line in Fig. 3.7 (0.5 keq/m^3). This means that it is possible to estimate the transport number ratio using the resistance obtained from a single-electrolyte solution, as I had predicted. However, the concentration of each electrolyte should be similar to that used to measure the electric resistance of the membrane, since the Donnan exclusion depends on the bulk concentration.

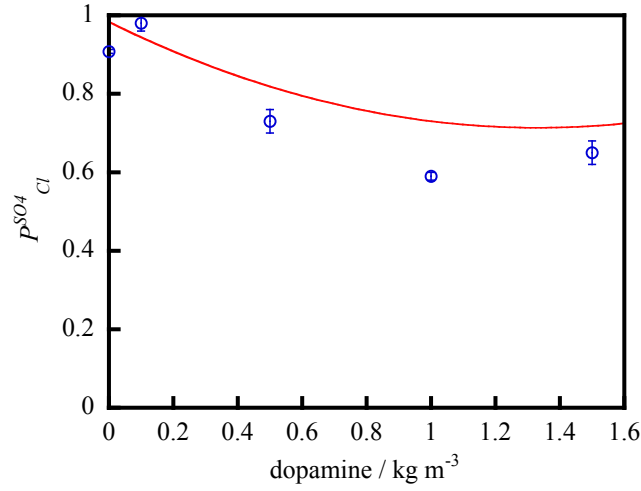


Fig. 3.7. Transport number ratio (P_{Cl}^{SO4}) for a mixture of NaCl and Na₂SO₄ (initial concentration of each electrolyte is 0.25 keq/m³). Symbols show the experimental data and the solid line shows the transport number ratio calculated with Eq. (3.3), using the membrane resistances shown in Table 3.1.

Table 3.1 Values of parameters used to calculate the solid line in Fig. 3.7.

Dopamine (kg/m ³)	Resistance for NaCl (Ω)			Resistance for Na ₂ SO ₄ (Ω)			P_{Cl}^{SO4}
	R_{Na}^{CMX}	R_{Cl}^A	$R_{dilu.}$	R_{Na}^{CMX}	R_{SO4}^A	$R_{dilu.}$	
0.0	0.5	0.65	16.75	0.5	1.75	16.27	0.97
0.1	0.5	1.50	16.75	0.5	2.75	16.27	0.96
0.5	0.5	1.75	16.75	0.5	6.20	16.27	0.83
1.0	0.5	2.45	16.75	0.5	10.70	16.27	0.72
1.5	0.5	2.35	16.75	0.5	10.35	16.27	0.72

R_{Na}^{CMX} : electric resistance of CMX for Na⁺; R_{Cl}^A and R_{SO4}^A : total electric resistance of AMX ($= R_{AMX}^{CMX} + R_{PDA}^{PDA}$) for Cl⁻ and SO₄²⁻, respectively; $R_{dilu.}$: electric resistance of diluted compartment due to corresponding electrolyte (NaCl or Na₂SO₄).

3.3.4. Analysis of experimental data

As discussed in Section 3.3.3, our theoretical predictions qualitatively agree well with the experimental results. However, it was impossible to estimate the transport

number ratio shown in Fig. 3.6. The experimental data shown in Fig. 3.6 was attempted to analyze in Fig. 3.6 by obtaining parameters necessary to theoretically estimate the transport number ratio of PDA-modified AMX for a given feed solution, since the electrolyte concentrations were much lower than those used to measure the electric resistance of AMX.

Referring to Eq. (2.9), the parameters that are required to estimate the transport number ratio are the electric resistance of CMX (R^{CMX}_{in}), that of modified AMX (R^A_{an}), and that of the diluted compartment ($R_{dilu.n}$). $R_{dilu.n}$ is obtained from the equivalent conductivity. R^{CMX}_{in} is obtained from the literature, as discussed in Section 3.3.3, because the cation is the same (Na^+) for all electrolytes. The only parameter I need is R^A_{an} , which is the sum of the resistance of AMX (R^{AMX}_{an}) and the resistance of the PDA layer (R^{PDA}_{an}).

It is found from Eq. (2.12) that by writing R^{AMX}_{anCgB} for R^{AMX}_{an} at any other concentration of an , meanwhile R^{AMX}_{anCcB} for R^{AMX}_{an} at a defined concentration of an which is obtained under specific experience, R^{AMX}_{anCgB} is given by Eq. (3.2).

$$\begin{aligned} R^{AMX}_{anCgB} &= \{ (l_M^A / \alpha_{an} U_{an} F M_s [an]_{gM}) / (l_M^A / \alpha_{an} U_{an} F M_s [an]_{cM}) \} R^{AMX}_{anCcB} \\ &= ([an]_{cM} / [an]_{gM}) R^{AMX}_{anCcB} \end{aligned} \quad (3.2)$$

where, $[an]_{cM}$ and $[an]_{gM}$ indicate the concentration of an partitioned into AMX from the diluted compartment of a defined concentration of an and of other concentration of an , respectively. R^{AMX}_{anCcB} can experimentally be measured, just like our measurement with the 0.5 keq/m³ electrolyte solution. The an concentration partitioned into AMX is given by Eqs. (2.2) and (2.3). $[an]_{cM}$ and $[an]_{gM}$ can be calculated if the membrane charge density of AMX (θ^{AMX}_M) is known.

The situation for the PDA layer is the same as that for AMX. If the charge density of PDA (θ^{PDA}_M) is known, the electric resistance of PDA at a given concentration, since the electric resistance of PDA for the 0.5 keq/m³ solution is already obtained.

The electric resistance of PDA-modified AMX will be the same as that of unmodified AMX, because I evaluated the transport number ratio at time zero, at which the bulk concentrations of feed solutions at both sides of the modified AMX are the same. Both surfaces of AMX are modified with PDA. The system at time zero is symmetric and the ion flux due to diffusion is zero. The ion concentration throughout the PDA layer and AMX is homogeneous. The electroneutrality condition is satisfied in the PDA layer and AMX. When I consider the Donnan equilibrium at the interface of a composite membrane like the PDA-modified membrane, I consider the hypothetical bulk layer between the PDA layer and AMX [35-37]. I then consider the Donnan equilibrium between the hypothetical bulk layer and the PDA layer, and that between the hypothetical bulk layer and AMX. The bulk concentration in the hypothetical bulk layer is obtained by adjusting the flux due to diffusion through the PDA layer to be the same as that through AMX. Under our conditions, the bulk concentration of the hypothetical bulk layer is the same as that of feed solution, since the distribution of electrolyte throughout the PDA layer is homogeneous. Then, the modified AMX is under the same conditions as unmodified AMX and the electric resistance of AMX itself (of modified AMX) is the same as that of unmodified AMX.

As discussed above, $R_{dil.u.n}$ is obtained from the equivalent conductivity and R_{in}^{CMX} is obtained from the literature. Of course, R_{in}^{CMX} will depend on the feed concentration. However, if the charge density of CMX (θ^{CMX}_M) is higher than the feed concentration, the amount of Na^+ partitioned into CMX is determined by θ^{CMX}_M to satisfy the electroneutrality condition, and will be almost equal to θ^{CMX}_M . Thus, it is reasonable to treat R_{in}^{CMX} as a constant for various feed concentrations. The membrane charge density of AMX can be estimated from the ion-exchange capacity and the water content of AMX to be 1.2 keq/m^3 [2]. Therefore, the only unknown parameter required to estimate the transport number ratio is the charge density of the PDA layer (θ^{PDA}_M). It was attempted to analyze $P^{SO_4}_{Cl}$ (shown in Fig. 3.6). Fig. 3.8 shows the theoretical curves of $P^{SO_4}_{Cl}$ calculated with Eq. (2.9) for various values of θ^{PDA}_M . It is found from Fig. 3.8 that θ^{PDA}_M is -0.14 keq/m^3 , based on the best fit of the theoretical curve with the experimental data. Table 3.2 shows the values of the parameters used to calculate the theoretical curve for line c in Fig. 3.8, in which θ^{PDA}_M is -0.14 keq/m^3 . All values are the same for all lines, except for R^{PDA} , which depends on θ^{PDA}_M .

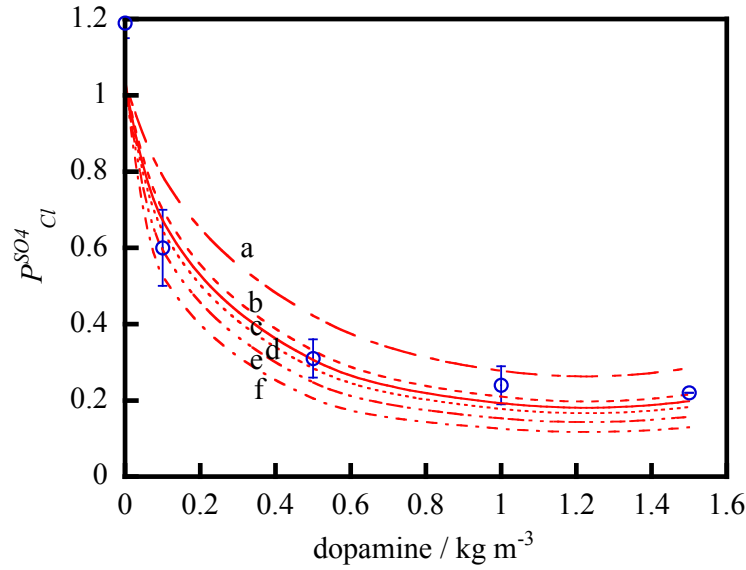


Fig. 3.8. Theoretical curves for P^{SO4}_{Cl} calculated with Eq. (3.3) for several charge densities of the PDA layer (θ^{PDA}_M). Symbols show the experimental data (also shown in Fig. 3.10). θ^{PDA}_M (in keq/m³) = -0.1 (a), -0.13 (b), -0.14 (c), -0.15 (d), -0.17 (e), and -0.2 (f).

Table 3.2 Values of parameters used to calculate the theoretical curve c ($\theta^{PDA}_M = -0.14$ keq/m³) in Fig. 3.8.

Dopamine (kg/m ³)	Resistance for NaCl (Ω)				Resistance for Na ₂ SO ₄ (Ω)				P^{SO4}_{Cl}
	R^{CMX}_{Na}	R^{AMX}_{Cl}	R^{PDA}_{Cl}	$R_{dilu.}$	R^{CMX}_{Na}	R^{AMX}_{SO4}	R^{PDA}_{SO4}	$R_{dilu.}$	
0.0	2	9.38	0.00	837.68	2	2.84	0.00	814.13	1.04
0.1	2	9.38	84.92	837.68	2	2.84	569.07	814.13	0.67
0.5	2	9.38	177.94	837.68	2	2.84	2532.40	814.13	0.31
1.0	2	9.38	291.17	837.68	2	2.84	5093.20	814.13	0.19
1.5	2	9.38	283.08	837.68	2	2.84	4894.00	814.13	0.20

R^{CMX} : resistance of CMX; R^{AMX} : resistance of AMX; R^{PDA} : Resistance of PDA layer; $R_{dilu.}$: resistance of diluted compartment.

In Table 3.2, the electric resistance of CMX is assumed to be $2 \times 10^{-4} \Omega \text{ m}^2$ [2] and it is 0.5Ω in our case, since the membrane area is $4 \times 10^{-4} \text{ m}^2$. In Fig. 3.8, the feed solution contains four electrolytes. There are four parallel circuits in the system. R^{CMX}_{Na} for each circuit is $2 \Omega (= 0.5 \Omega \times 4)$.

Fig. 3.9 shows the theoretical curves calculated with $\theta^{PDA}_M = -0.14 \text{ keq/m}^3$ for the experimental data shown in Fig. 3.6. Tables 3.3 and 3.4 show the values of the parameters used to calculate the theoretical curves for $P^{NO_3}_{Cl}$ and P^F_{Cl} , respectively. It is found from Fig. 3.9 that the theoretical curves fit the experimental data very well and the theory can quantitatively explain the experimental data. It is also found that the charge density of the modified layer can be estimated with our model.

It is found from Tables 3.2– 3.4 that the transport number ratio is mostly determined by the electric resistances of the diluted compartment and the PDA layer. Comparing Table 3.2 with Tables 3.3 and 3.4, it is found that the electric resistance of the PDA layer for SO_4^{2-} is much higher than those for Cl^- , NO_3^- , and F^- . This is because, as discussed in Chap. 2, the Donnan exclusion (by the PDA layer) of SO_4^{2-} is much higher than that of Cl^- , NO_3^- , and F^- . In addition, for $P^{SO_4}_{Cl}$, the electric resistance of the PDA layer for SO_4^{2-} becomes higher than that of the diluted compartment for SO_4^{2-} with an increase in the concentration of dopamine. Thus, the ion flux of SO_4^{2-} is mainly determined by the electric resistance of the PDA layer, and $P^{SO_4}_{Cl}$ decreases with an increase in the concentration of dopamine in the modification solution.

In Tables 3.3 and 3.4, the electric resistances of PDA layer for Cl^- , NO_3^- and F^- are lower than those of the diluted compartment due to NaCl, NaNO₃ and NaF, respectively, under the experimental conditions. In addition, $R^{PDA}_{NO_3}/R^{PDA}_{Cl}$ and

R^{PDA}_F/R^{PDA}_{Cl} hardly depend on the concentration of dopamine. The effect of the charge density of the PDA layer on the partitioning of ions is the same for Cl^- , NO_3^- , and F^- , because the ionic charges of these ions are the same, as discussed in Chap. 2. The transport number ratio between monovalent anions is hardly affected by the modification of the surface of AMX with a negatively charged layer.

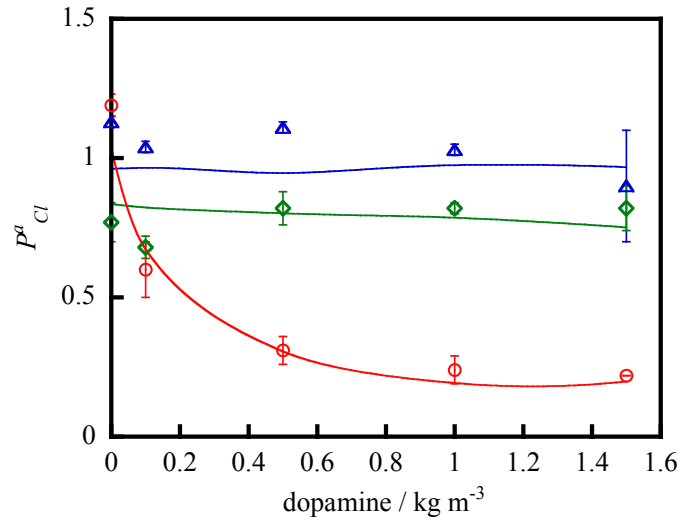


Fig. 3.9. Theoretical curves calculated with Eq. (2.9) (using $\theta^{PDA}_M = -0.14 \text{ keq/m}^3$) as a function of the concentration of dopamine. In this figure, the feed solution is a mixture of NaCl, NaF, NaNO₃, and Na₂SO₄, with an initial concentration of 0.01 keq/m³ of each electrolyte. Symbols show the experimental data. Δ : $P^{NO_3}_{Cl}$; $\diamond$: P^F_{Cl} ; $\circ$: $P^{SO_4}_{Cl}$.

Table 3.3 Values of parameters used to calculate the theoretical curve for P^{NO3}_{Cl} in Fig. 3.9.

Dopamine (kg/m ³)	Resistance for NaCl (Ω)				Resistance for NaNO ₃ (Ω)				P^{NO3}_{Cl}
	R^{CMX}_{Na}	R^{AMX}_{Cl}	R^{PDA}_{Cl}	$R_{dilu.}$	R^{CMX}_{Na}	R^{AMX}_{NO3}	R^{PDA}_{NO3}	$R_{dilu.}$	
0.0	2	9.38	0.00	837.68	2	9.38	0.00	871.41	0.97
0.1	2	9.38	84.92	837.68	2	9.38	84.92	871.41	0.95
0.5	2	9.38	177.94	837.68	2	9.38	202.20	871.41	0.97
1.0	2	9.38	291.17	837.68	2	9.38	287.13	871.41	0.97
1.5	2	9.38	283.08	837.68	2	9.38	287.13	871.41	0.97

R^{CMX} : Resistance of CMX; R^{AMX} : resistance of AMX; R^{PDA} : Resistance of PDA layer; $R_{dilu.}$: Resistance of diluted compartment.

Table 3.4 Values of parameters used to calculate the theoretical curve for P^F_{Cl} in Fig. 3.9.

Dopamine (kg/m ³)	Resistance for NaCl (Ω)				Resistance for NaF (Ω)				P^F_{Cl}
	R^{CMX}_{Na}	R^{AMX}_{Cl}	R^{PDA}_{Cl}	$R_{dilu.}$	R^{CMX}_{Na}	R^{AMX}_F	R^{PDA}_F	$R_{dilu.}$	
0.0	2	9.38	0.00	837.68	2	11.11	0.00	1003.70	0.84
0.1	2	9.38	84.92	837.68	2	11.11	118.09	1003.70	0.82
0.5	2	9.38	177.94	837.68	2	11.11	263.67	1003.70	0.80
1.0	2	9.38	291.17	837.68	2	11.11	433.52	1003.70	0.79
1.5	2	9.38	283.08	837.68	2	11.11	490.14	1003.70	0.75

R^{CMX} : Resistance of CMX; R^{AMX} : resistance of AMX; R^{PDA} : Resistance of PDA layer; $R_{dilu.}$: Resistance of diluted compartment.

Fig. 3.10 shows the theoretical curves calculated with $\theta^{PDA}_M = -0.14$ keq/m³ for the experimental data shown in Fig. 3.7. Table 3.5 shows the values of the parameters used to calculate the theoretical curve for P^{SO4}_{Cl} . In this figure, the feed solution contains 0.25 keq/m³ NaCl and 0.25 keq/m³ Na₂SO₄. The system contains two parallel circuits; R^{CMX}_{Na} for each circuit is 1 Ω ($= 0.5 \Omega \times 2$). It is found from Fig. 3.10 that the theoretical curve does not fit the experimental data well. The theoretical curve shown in

Fig. 3.10 is almost same as the solid line in Fig. 3.7 that was calculated with the electric resistances corresponding to a 0.5 keq/m^3 single-electrolyte solution. The theoretical membrane resistance (Eq. (2.12)) was derived under the assumption that the membrane charge densities of AEM and CEM are much higher than the feed solution. However, the total feed concentration in Figs. 3.7 and 3.10 is 0.5 keq/m^3 , which is about half of the membrane charge density (estimated membrane charge density of AMX is 1.2 keq/m^3). This is the main reason for the discrepancy between the theoretical curve and the experimental data in Fig. 3.10. However, the theoretical curve fits the experimental data within an error of about ± 0.1 . The discrepancy between the theoretical curve and the experimental data in Fig. 3.10 may be an acceptable one.

It is found from Table 3.5 that $R^{PDA}_{SO_4}$ becomes much higher than R^{PDA}_{Cl} with an increase in the concentration of dopamine. However, R^{PDA}_{Cl} and $R^{PDA}_{SO_4}$ are lower than the electric resistances of the diluted compartment due to NaCl and Na_2SO_4 , respectively. Therefore, the effect of the electric resistance of the PDA layer on the transport number ratio is not as strong as the effect on $P^{SO_4}_{Cl}$ shown in Fig. 3.9. In other words, the effect of the electric resistance of the diluted compartment is larger than that of the PDA layer in Fig. 3.9. The transport number ratio $P^{SO_4}_{Cl}$ in Fig. 3.10 is larger than that in Fig. 3.9; that is, the selectivity for monovalent anions in Fig. 3.10 is lower than that in Fig. 3.9. This is because the feed concentration in Fig. 3.10 is higher than that in

Fig. 3.9. The effect of the charge density on the Donnan exclusion in Fig. 3.10 is smaller than that in Fig. 3.9.

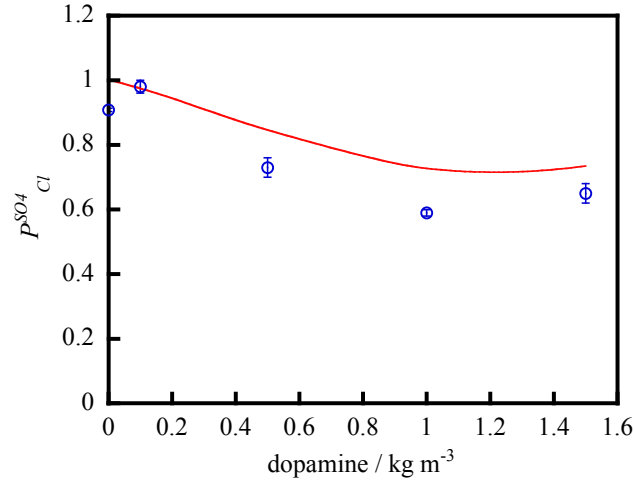


Fig. 3.10. Theoretical curve calculated with Eq. (2.9) (using $\theta^{PDA}_M = -0.14$ keq/m³) as a function of the concentration of dopamine. In this figure, the feed solution is a mixture of 0.25 keq/m³ NaCl and 0.25 keq/m³ Na₂SO₄. Symbols show the experimental data.

Table 3.5 Values of parameters used to calculate the theoretical curve for P^{SO4}_{Cl} in Fig. 3.10.

Dopamine (kg/m ³)	Resistance for NaCl (Ω)				Resistance for Na ₂ SO ₄ (Ω)				P^{SO4}_{Cl}
	R^{CMX}_{Na}	R^{AMX}_{Cl}	R^{PDA}_{Cl}	$R_{dilu.}$	R^{CMX}_{Na}	R^{AMX}_{SO4}	R^{PDA}_{SO4}	$R_{dilu.}$	
0.0	1	1.83	0.00	33.50	1	2.71	0.00	32.54	1.00
0.1	1	1.83	1.03	33.50	1	2.71	2.07	32.54	0.98
0.5	1	1.83	2.15	33.50	1	2.71	9.22	32.54	0.85
1.0	1	1.83	3.51	33.50	1	2.71	18.55	32.54	0.73
1.5	1	1.83	3.42	33.50	1	2.71	17.82	32.54	0.74

R^{CMX} : Resistance of CMX; R^{AMX} : resistance of AMX; R^{PDA} : Resistance of PDA layer; $R_{dilu.}$: Resistance of diluted compartment.

In our experiment, the thickness of the diluted compartment is about 100 times higher than that of a practical ED system (0.75 mm) [38]. In a practical ED system, the electric resistance of the diluted compartment will be around 100 times lower than that of our system (shown in the tables). This means that the transport number ratio $P^{SO_4}_{Cl}$ in the practical ED system will be smaller than those shown in Figs. 3.6 and 3.7. For example, $P^{SO_4}_{Cl}$ goes from 0.73 to 0.30 for the AMX modified with 1 kg/m³ dopamine (Table 3.5) if the electric resistance of the diluted compartment decreases by a factor of 100. Regarding the membrane resistance, the electric resistance of AMX was increased (up to 10–15 Ω cm² for monovalent anions and up to more than 40 Ω cm² for sulfate) by PDA modification as shown in Fig.3.4. In principle, the energy consumption will be increased by PDA modification. However, in practical ED system, the membrane area is about 0.7 m² [38]. So, the electric resistance of membrane is about 0.0057 Ω even if the membrane resistance is 40 Ω cm². Then, the increase of electric resistance of ion exchange membrane does not affect the energy consumption of ED system so much. Therefore, it is clear that the modification of the surface of an AEM with a negatively charged layer is a very useful method to improve the selectivity for monovalent anions in the ED process. The surface modification of AEM with PDA is very easy and effective.

It is reasonable to consider that the charge density of CMX (θ^{CMX}_M) is comparable to that of AMX (θ^{AMX}_M), because the ion exchange capacity of CMX is comparable to that of AMX [2]. The charge density of the PDA layer (θ^{PDA}_M) is -0.14 keq/m³; it is not too high and about ten times lower than θ^{CMX}_M . If θ^{PDA}_M is comparable to θ^{CMX}_M , the PDA layer acts as a CEM and anions do not partition into the PDA layer. In addition,

the electric resistance of the PDA layer is high enough, even though the PDA layer is very thin. The thickness of the PDA layer is in the order of 10 nm [33], while the thickness of AMX is around 0.15 mm. Thus, the modification of the surface with PDA brought about excellent results with regard to the improvement of the selectivity for monovalent anions.

3.4. Conclusion

In previous chapter, I theoretically discussed the effect of several parameters of the system (including the AEM) on the selectivity for monovalent anions in order to understand this selectivity. In this chapter, I modified an anion exchange membrane with polydopamine in order to experimentally verify the theoretical discussion and predictions. Polydopamine provided a negatively charged layer on the anion exchange membrane surface. I measured the permselectivities of the PDA-modified AEM for NO_3^- , F^- , and SO_4^{2-} relative to Cl^- .

It was found that the theoretical predictions match the experimental results and the validity of our theoretical model was confirmed. The selectivity for monovalent anions was improved by the modification of the surface of AEM, as expected from theoretical considerations. The permselectivity between monovalent anions was not affected by the surface modification.

In addition, I analyzed the experimental data with our theoretical model and showed that I could determine the charge density of the negatively charged layer on the surface of the AEM. The theoretical curves calculated with the obtained charge density of the negatively charged layer fit the experimental results well. It was showed that the selectivity for monovalent anions is determined mainly by the electric resistances of the

negatively charged layer and the diluted compartment. The electric resistance of the diluted compartment in a real ED system is lower than that of our system in this paper. Therefore, in a practical ED system, it is expected that the selectivity for monovalent anions will be higher than that shown in this study. It makes clear that the modification of the surface of the AEM with a negatively charged layer is a very useful method to improve the selectivity of the ED process for monovalent anions.

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Chapter 4

Improved antifouling of anion-exchange membrane by polydopamine coating in electrodialysis process

4.1. Introduction

Water is one of the most precious and important resources for all living creatures. Nevertheless, the drinking water shortage has been serious problem throughout the world. Oki and Kanae reported in 2006 that more than two billion people live in water-stressed areas [1]. Membrane processes, such as reverse osmosis (RO), nanofiltration (NF) and electrodialysis (ED), are widely used to produce drinking water from seawater, brackish water and wastewater. Among these, ED was justified for the treatment of more dilute brackish water from an energy efficiency point of view [2]. On the other hand, it has reported that ED is fully suitable for seawater desalination and may compete with RO and thermal methods [3].

Electrodialysis is an electrochemical separation process that uses cation and anion exchange membranes [4]. In ED process, ions are selectively transported from one compartment (diluted compartment) to another (concentrated compartment) through ion exchange membranes under an electrochemical potential gradient. An applied direct

current (DC) voltage is the main driving force in ED process [5]. The advantages of ED compared with RO and NF are its high water recovery, the long useful life of membrane (because of their high chemical and mechanical stability) and the possibility of operation at temperatures up to 50°C [4]. In addition, ED is effective for removing harmful ions such as NO_3^- and F^- effectively from feed water [6-13]. Infants younger than 6 months old are susceptible to nitrate poisoning which compromises the blood's ability to carry oxygen [14]. A high concentration of F^- in drinking water results in fluorosis (dental/skeletal abnormalities) and several types of neurological damage [12].

In spite of such advantages, fouling, in particular the fouling of anion exchange membranes (AEMs), is a major obstacle even in ED process, since AEM has positive charge and most organic foulants, such as surfactants, humates and proteins, are negatively charged. Fouling increases a membrane resistance and decreases a system performance. Some attempts to increase the antifouling potential of AEMs have reported [15, 16]. I have also reported that the antifouling potential of AEM is improved by the surface modification with polyelectrolytes [17-19] because of increased of hydrophilicity and negative surface charge density.

Recently, a surface modification with polydopamine (PDA) has attracted significant attention for improving the antifouling potential of membranes [20-23]. Dopamine is readily oxidized in an aerobic, alkaline aqueous solution and spontaneously polymerizes to form a cross-linked PDA. PDA is a bio-inspired polymer (i.e. bio-glue) that deposits non-selectively from solution onto virtually any solid surface [24] and is hydrophilic [25]. Xi et al. reported that the hydrophilicity of polyethylene, poly (vinylidene fluoride) (PVDF) and poly(tetrafluoroethylene) porous

membranes was significantly improved by surface modification with PDA [20]. It has been reported that bovine serum albumin (BSA) adhesion to a polysulfone ultrafiltration membrane, PVDF microfiltration membrane and a polyamide RO membrane was reduced by at least 96% through PDA deposition [22]. PDA is amphoteric with a reported isoelectric point of around pH 4 [26, 27]. Polymer layers containing hydroxyl and amino groups are attached to membranes by strong interactions between PDA and membrane surfaces [20].

The experimental results mentioned above encouraged us to attempt modification of AEMs with PDA in the expectation that hydrophilicity and negative surface charge density of AEM would be increased with PDA coating. The improvement of hydrophilicity and the increasing of negative charge density are dominant factors in improving antifouling potential against organic foulants [17, 28-30]. In addition, the PDA layer on AEM surface is expected to be highly stable, since PDA is expected to strongly attach to the membrane surface [24]. Furthermore, recently, PDA has attracted considerable interest recently for various types of biomedical applications [31] indication that PDA can be used safely to modify membranes for producing drinking water. Thus, in this chapter, I attempt to modify AEM surface with PDA to improve the antifouling potential. The optimal modification condition and the phycochemical mechanism behind improved antifouling potential are discussed.

4.2. Experimental

4.2.1. Materials

A NEOSEPTA AMX membrane (Astom Corp., Tokyo, Japan), which has strongly basic anion exchange groups, was used as the AEM. The characteristic properties of this membrane were as follows: electrical resistance 2.0×10^{-4} to $3.5 \times 10^{-4} \Omega \text{ m}^2$, and exchange capacity 1.4 – 1.7 eq/kg of dry membrane [32]. Dopamine hydrochloride (Sigma-Aldrich, Tokyo, Japan) was used to modify the AEM membrane surfaces. Sodium dodecyl benzene sulfonate (SDBS, Sigma-Aldrich) was used as a model organic foulant and NaCl (Wako Pure Chemicals Inc., Osaka, Japan) as an electrolyte in ED. All chemicals were used as received and Milli-Q water (Millipore, Bedford, MA, USA) was used in all experiments.

The chemical structures of dopamine and SDBS are shown in Fig. 4.1. SDBS is a model organic foulant commonly used to investigate fouling of AEMs in ED process [33-35] and it remains negatively charged over the entire pH range. Figure 4.2 shows the formation and structure of PDA. PDA is spontaneously formed from an aerobic and alkaline dopamine aqueous solution. In Fig. 4.2, -OH groups dissociate to be -O^- and -NH dissociates to -NH_2^+ depending on pH. Thus, PDA is a kind of amphoteric substance. The isoelectric point, I_{sp} of PDA is reported to be around pH 4 [26, 27]. PDA is negatively charged in ED process for producing drinking water, since the pH range of drinking water is between pH 6.5 and 8.5 [36].

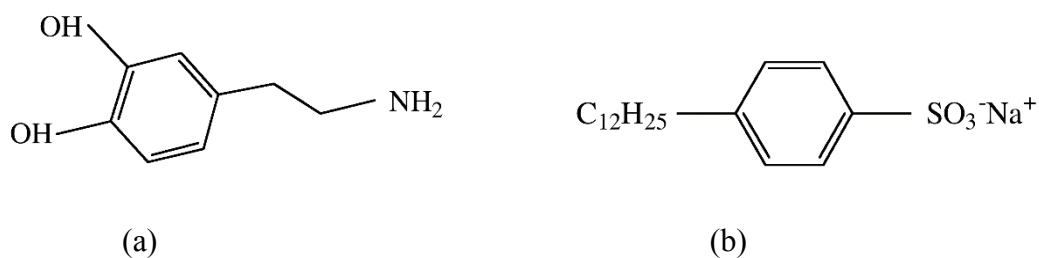


Fig. 4.1. Chemical structure of (a) dopamine and (b) SDBS.

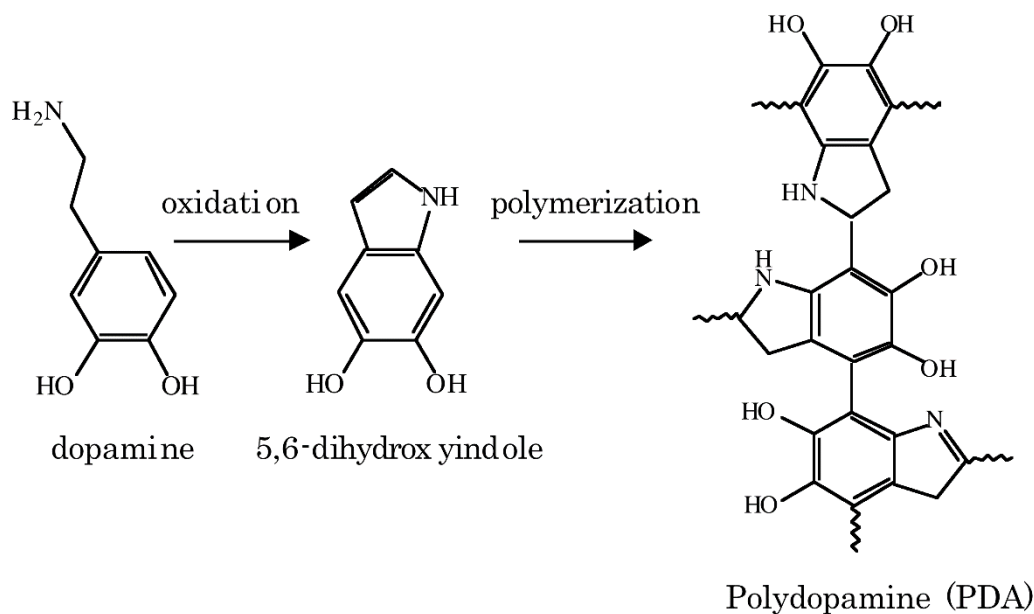


Fig. 4.2. Polydopamine formation [24, 25].

4.2.2 Membrane modification

Dopamine solution used for surface modification was prepared by dissolving a desired amount of dopamine in 15 mM Tris-HCl buffer (pH8.8). A freshly prepared dopamine solution is clear. But, it begins to change color immediately from clear to darkish brown through contact with oxygen in the air, indicating the formation of PDA.

The AMX membrane was immersed vertically in the freshly prepared dopamine solution in contact with atmospheric oxygen at 30°C for a desired time. The concentration of dopamine and the immersion time were varied for experiments. After modification, the membrane was rinsed thoroughly with Milli-Q water for one day. The modified membranes were kept in Milli-Q water until required. The color of AMX membrane became darkish brown through deposition of PDA on the surface as shown in Fig 4.3.

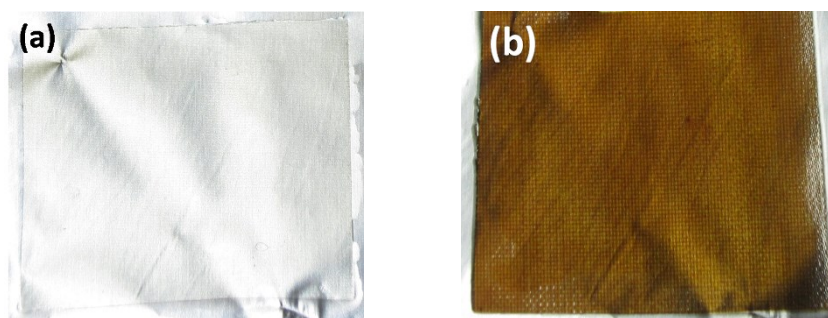


Fig. 4.3. The color of AMX (a) before and (b) after modification with 0.1 kg/m³ dopamine solution.

4.2.3 Characterization

The water contact angle and the ζ -potential of the modified membrane surface were measured to characterize the membrane surface. The contact angle was measured with a contact angle meter, CA-A (Kyowa Interface Science Co. Ltd., Saitama, Japan) by dropping 0.5 μ l of water onto the membrane surface. The measurement was repeated at least twenty times for each sample and the mean value was obtained. The ζ -potential was obtained from the streaming potential measurement by an ELS-4000K instrument (Otsuka Electronics, Osaka, Japan) using 0.01 kg/m³ NaCl solution (pH 6.2) at room

temperature. The ζ -potential measurement was repeated at least three times for each sample and mean values were obtained.

The surface morphologies of the original and modified membranes were observed by a field scanning electron microscope (FE-SEM, JSF-7500F, JEOL Co. Ltd., Tokyo, Japan) with an accelerating voltage of 5 kV. The membrane samples were first dried in a freeze drier (FDU-1200 EYELA, Tokyo Rikakikai Co. Ltd., Tokyo, Japan) overnight and then, coated with osmium tetroxide by osmium coater (NEOC-STBMEWAFOSIS Co., Ltd., Tokyo, Japan)

4.2.3. Evaluation of antifouling potential

The antifouling potential was evaluated using the method in our previous studies [17-19]. Figure 4.4 shows the experimental setup to measure the fouling behavior. In the setup shown in Fig. 4.4, the diluted compartment is on the left hand side and the concentrated compartment is on the right. The effective membrane area was $4 \times 10^{-4} \text{ m}^2$ ($0.02 \times 0.02 \text{ m}$) and the volume of each compartment was $1 \times 10^{-4} \text{ m}^3$. The feed solution contained 0.05 M NaCl and a given concentration of SDBS (kg/m^3). The pH of feed solution was not adjusted and was pH 6.2. The feed solution was circulated from the reservoir through both compartments at a flow rate of $1.2 \times 10^{-3} \text{ m}^3/\text{min}$ at $30 \pm 1 \text{ }^\circ\text{C}$. Thus, the composition of the feed solution was held constant during the experiment. The applied DC current density was constant at 20 A/m^2 , giving a total of 8 mA. The time course of voltage across the membrane during the fouling experiment was measured with Ag-AgCl electrodes placed close to the membrane surfaces and was recorded with a data logger.

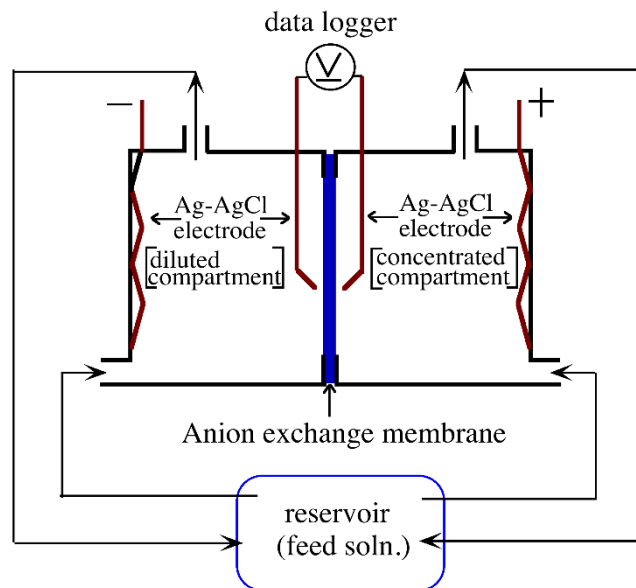


Fig. 4.4. Experimental setup for fouling experiments.

Figure 4.5 shows an example of experimental data. Generally, the fouling proceeds via several steps [35]. We divide it into the three steps as shown in Fig. 4.5(a). The first step is the start-up time for fouling and the second step is a period of fouling progress. In the third step, the fouling is complete and membrane will be unusable. The fouling takes place at the end of the first step as shown in Fig. 4.5(b). Thus, in this study, I focused on the first step to evaluate the antifouling potential of AEM. When fouling occurs, the voltage across the membrane, ΔE , increases, since the electrical resistance of the membrane increases under a constant electric current. In the absence of fouling, ΔE is constant, because the composition of the feed solution does not change during the experiment. As shown in Fig. 4.5(b), ΔE initially gradually increases during ED due to the increase in SDBS concentration in a thin region closed to the membrane surface called the surface layer (i.e. an increase in electrical resistance of the surface layer) and the adsorption of a small amount of SDBS micelles. A small amount of micelles can

exist in the solution, even though the concentration is below the critical micelle concentration (CMC). Subsequently, ΔE increases rapidly after the fouling takes place. The time elapsed until the occurrence of fouling is called the transition time, t_{tran} . The transition time is long when little fouling takes place, but is short when fouling occurs readily. Thus, the transition time was used as a parameter that reflects the antifouling potential of the AEM.

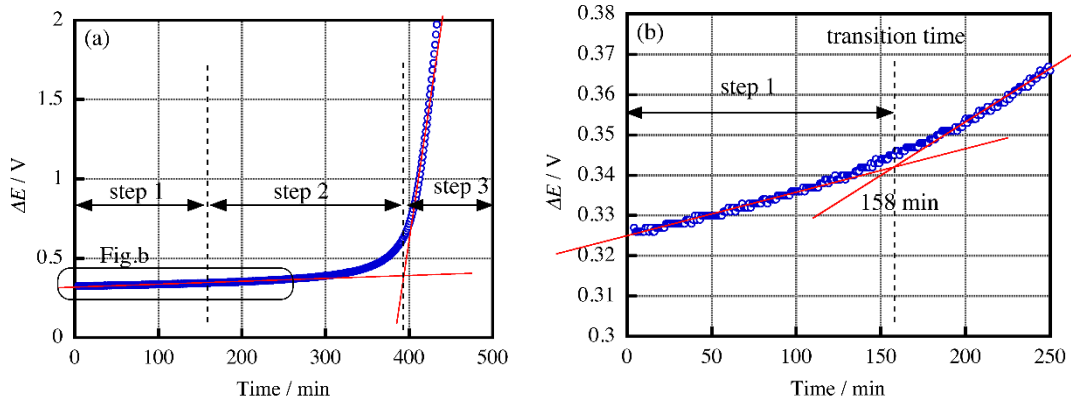


Fig. 4.5. The potential difference across the membrane and the determination of transition time. The feed solution (pH6.2) contained 0.05 M NaCl as an electrolyte and 0.052 kg/m³ SDBS as a foulant. The membrane was modified with 0.05 kg/m³ dopamine solution at pH 8.8 for 24 h.

4.3. Results and discussion

4.3.1. Optimal conditions for surface modification

4.3.1.1. Optimal modification time

To find the optimal modification time, the water contact angle of modified AMX membrane was measured as a function of time, using 1 and 2 kg/m³ dopamine solutions. As shown in Fig. 4.6, the contact angle decreased sharply during first 12 h and became

almost constant after 24 h. The decrease in contact angle indicates an increase in hydrophilicity of the membrane surface. This will be caused by an increase in the number of hydrophilic groups on the membrane surface, since PDA has a lot of $-OH$ and $>NH$ groups. The adsorption of PDA was almost in an equilibrium state after 24 h. Thus, 24 h was determined as the optimal modification time.

In addition, it was found that the contact angle of the membrane modified with 1 kg/m^3 dopamine solution was almost same as that modified by 2 kg/m^3 dopamine solution. Thus, 1 kg/m^3 would be sufficient for saturated adsorption of PDA.

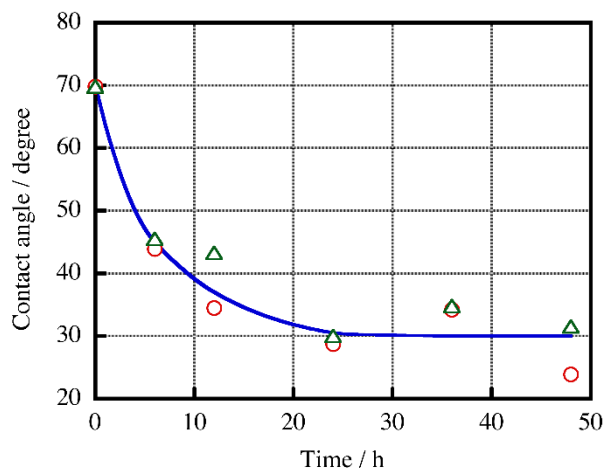


Fig. 4.6. Water contact angle of a modified AMX membrane as a function of deposition time. Circles correspond to an AMX modified by 1 kg/m^3 dopamine and triangles by 2 kg/m^3 dopamine.

4.3.1.2. Optimal concentration of dopamine

Figures 4.7(a) and 4.7(b) show the ζ -potential and the water contact angle, respectively, of modified AMX membranes as a function of dopamine concentration of dopamine solution. It can be found from Fig. 4.7(a) that the absolute value of negative ζ

-potential increased (negative charge density increased) with dopamine concentration, and became constant above 0.5 kg/m^3 . The increase in negative ζ -potential indicates an increase in electrostatic repulsion between foulants with a negative charge and the membrane surface charge, which indicates an improved antifouling potential.

In addition, from Fig. 4.7(b), the water contact angle decreased with increasing dopamine concentration and became constant above 1 kg/m^3 dopamine. The decrease in contact angle corresponds to an increase in hydrophilicity of the membrane surface. It is known that a hydrophilic membrane potentially shows better antifouling potential for hydrophobic foulants [37].

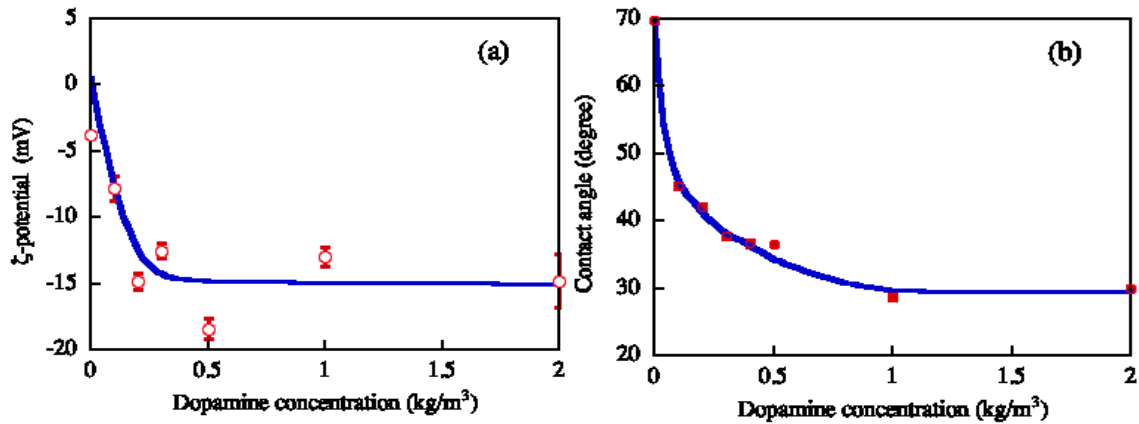


Fig.4.7. ζ -potential and water contact angle of modified AMX membrane as a function of dopamine concentration.

Both ζ -potential and water contact angle became constant above 1 kg/m^3 dopamine. These phenomena consistent with Fig. 4.6. That is, 1 kg/m^3 dopamine is sufficient to saturate the PDA adsorption. Thus, it was expected that the antifouling potential would improve with dopamine concentration and became constant above 1 kg/m^3 dopamine.

Figure 4.8 shows the transition time as a function of dopamine concentration. In Fig. 4.8, the feed solution contained 0.052 kg/m^3 SDBS and 0.05 M NaCl . This SDBS concentration was about three times higher than the CMC ($1.74 \times 10^{-2} \text{ kg/m}^3$) of SDBS [17] and corresponds to a condition where the fouling takes place very readily. As shown in Fig. 4.8, the transition time of the unmodified membrane (the first data point in Fig. 4.8) was zero under this condition. It is found from Fig. 4.8 that, contrary to our expectation mentioned above, the transition time showed a maximum at around 0.1 kg/m^3 and above this point, decreased sharply with the dopamine concentration. Thus, the optimal concentration of dopamine was 0.1 kg/m^3 .

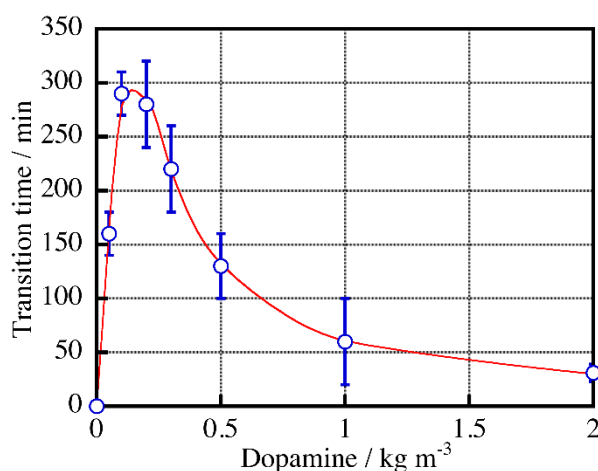


Fig. 4.8. Transition time as a function of dopamine concentration. The data at 0 kg/m^3 dopamine corresponds to the unmodified membrane. The feed solution contained 0.052 kg/m^3 SDBS and 0.05 M NaCl and its pH was 6.2.

The transition time decreased sharply above 0.1 kg/m^3 , in spite of the increase in negative surface charge density and the hydrophilicity with the dopamine concentration. To consider the reason behind this phenomenon, the SEM images of the membrane

surface were taken to confirm the morphology changes of the membrane surface arising from modification with PDA. Figure 4.9 shows the SEM images of unmodified and modified AMX membranes. It is found from Fig. 4.9 that the particle size of PDA deposited on the membrane surface increased with increasing dopamine concentration. For membranes modified with more than 1 kg/m^3 dopamine solution, the some particles aggregated on the membrane surface. It is reported that the thickness of the PDA layer increases with the PDA concentration and deposition time [38, 39]. The thickness of the PDA layer was reported as about $0.11 \text{ }\mu\text{m}$ for monocrystalline silicon chip coated with 2 kg/m^3 dopamine solution for 24 h at pH 8.5 [38]. For AMX membrane modified with 2 kg/m^3 dopamine solution at pH 8.8 for 24 h (Fig. 4.9(f)), the thickness of the PDA layer may be a little bit thicker than this value, estimating from the particle size shown in Fig. 4.9. The thickness of the PDA layer for other modified AMX membranes will be thinner than $0.11 \text{ }\mu\text{m}$. Consequently, the roughness of the membrane surface increased with increasing dopamine concentration. It is known that the antifouling property for rough surfaces is lower than for smooth surfaces [40, 41]. The decrease in transition time (the decrease in antifouling potential) was probably due to this increase in membrane surface roughness. Thus, the optimal concentration was determined through the competition between the increase in antifouling potential due to the increase in negative charge density and hydrophilicity of membrane surface and the decrease in antifouling potential due to the increase in membrane surface roughness. Consequently, 0.1 kg/m^3 was an optimal concentration of dopamine solution for improving antifouling potential of anion exchange membrane. The transition time was about 300 min under the optimum condition (modification with 0.1 kg/m^3 dopamine solution at pH 8.8 for 24 h).

This value was longer than AMX modified with polyanion, but shorter than ACS (monovalent selective AEM, Astom Corp.) modified with polyanion [17–19]. Kusumoto et al. attempted to increase the antifouling potential of AEM by introducing carboxylic acid group onto the membrane surface [16]. The antifouling potential of their membranes were higher than ours, while their modification procedure was complicated compared with ours. Hence, the surface modification with dopamine is not the best but it is a very simple and effective way to improve the antifouling potential of AEM. It is easily considered that the membrane resistance increases with the increase of PDA layer thickness. I measured the membrane resistance from the difference of cell resistance between with and without membrane at 1 kHz with 0.5 M NaCl aqueous solution. The membrane resistance of unmodified membrane was $(2.51 \pm 0.08) \times 10^{-4} \Omega\text{m}^2$ and $(5.0 \pm 0.1) \times 10^{-4} \Omega\text{m}^2$ for the membrane modified with 0.1 kg/m³ dopamine solution. In addition, it would be expected that the monovalent selectivity would increase with the PDA coating, because the monovalent selectivity is increased with the increase in the total amount of negative charge within the surface layer [18].

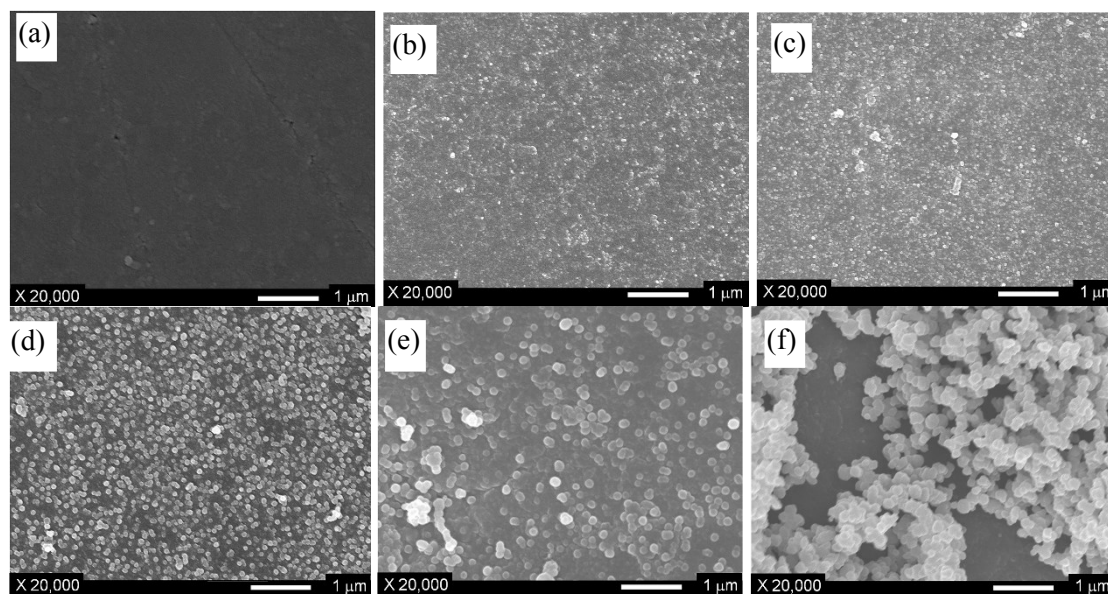


Fig. 4.9. FE-SEM images of membrane surface modified with (a) 0 kg/m³ (unmodified membrane), (b) 0.1 kg/m³, (c) 0.3 kg/m³, (d) 0.5 kg/m³, (e) 1 kg/m³ and (f) 2 kg/m³ dopamine solution.

4.3.2. Evaluation of antifouling potential

Figure 4.10 shows the transition time of unmodified and modified AMX membranes as a function of SDBS concentration. It is found from Fig. 4.10 that the transition time for the unmodified membrane was almost zero above the CMC of SDBS. This means the fouling takes place immediately after the beginning of ED when the SDBS concentration is higher than CMC. This result agrees with the report that fouling by SDBS is promoted by micelles [35]. On the other hand, the transition time for modified membrane was extremely longer than that for the unmodified membrane over the entire range of SDBS concentrations although it decreased with increasing SDBS concentration. The transition time was still long even above the CMC. Thus, it is clear that the surface modification with PDA sufficiently improved the antifouling potential of the anion exchange membrane.

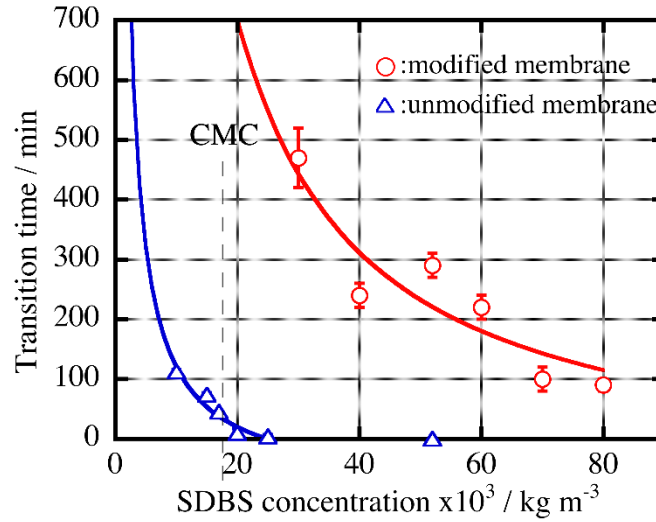


Fig. 4.10. Transition time of modified and unmodified AMX membranes as a function of SDBS concentration in the feed solution (pH6.2). Circles show the modified membrane and triangles the unmodified membrane. The membrane was modified with 0.1 kg/m³ dopamine solution at pH 8.8 for 24 h. The feed solution contained 0.05M NaCl and SDBS. Solid lines show the theoretical curves calculated by Eq. (4.1) using the parameters shown in Table 4.1.

The data shown in Fig. 4.10 were analyzed with the previously described theoretical model [17] shown in Fig. 4.11 to clarify the mechanism behind improvement in antifouling potential. In this model, a thin surface layer of thickness δ (m) is assumed on the membrane surface. SDBS in the feed solution moves into the surface layer through electrophoretic migration under the influence of an electric field, E (V/m). When the SDBS concentration in the surface layer exceeds the CMC, micelles are formed within the surface layer and are adsorbed on the membrane surface, causing fouling. According to this model, the transition time (s) is given by Eq. (4.1).

$$t_{tran} = \{(CMC + \alpha) \delta / (u E C_{SDBS}^f)\} - \delta / (u E) \quad (4.1)$$

Here, $(CMC + \alpha)$ (kg/m³) denotes the concentration of SDBS in the surface layer when the fouling takes place, u the electrophoretic mobility of SDBS (m²/sV) and C_{SDBS}^f the SDBS concentration in the feed (kg/m³). The solid lines shown in Fig. 4.10 show the

theoretical curves calculated with Eq. (4.1) using the parameters shown in Table 4.1. The values of parameters were determined from the best fit of the theoretical curves with the experimental data. The value of $\delta/(u E)$ does not depend on the membrane properties, but is determined by the foulant. Thus, this value is same for unmodified and modified membranes and is also the same as that in our previous work in which SDBS was used as the foulant [17]. It is clear that the theoretical curves fit with the experimental data very well. According to this model, when α is small, the fouling takes place readily, but when α is large, little fouling takes place. A large value of α indicates that the micelles are scarcely adsorbed and consequently, that the membrane has a high antifouling potential.

From Table 4.1, the value of α for the unmodified membrane is $7.6 \times 10^{-3} \text{ kg/m}^3$ and is 0.178 kg/m^3 for the modified membrane. Thus, it is clear that the surface modification with PDA prevented the adsorption of SDBS micelles onto the membrane surface and sufficiently improved the antifouling potential of the AEMs. This sufficient improvement was due to the increase in negative charge density and hydrophilicity of the membrane surface, which overcame the negative effect of increased membrane surface roughness.

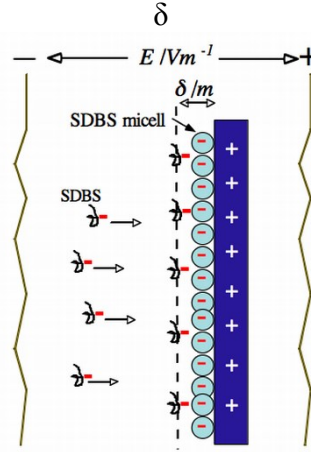


Fig. 4.11. Model of the fouling mechanism due to SDBS [17]. E denotes the applied DC voltage and δ is the thickness of the surface layer.

Table 4.1 Parameters used in the analysis of Fig. 4.10.

	$CMC+\alpha$ (kg/m ³)	α (kg/m ³)	δ/uE (s)
modified	0.195	0.178	4800
unmodified	2.5×10^{-2}	7.6×10^{-3}	4800

4.3.3. Stability of the modified membrane

I investigated the stability of PDA modified membrane in Milli-Q water considering a storage condition. In addition, during practical ED operation, PDA coating is a kind of fouling for AEM. The PDA particles have a negative charge and are under influence of applied DC voltage. The deposited PDA particles are always pressed against the membrane surface. Thus, the PDA layer will be stable in the practical ED operation.

The transition time was measured after the modified membrane was kept in Milli-Q water for givens periods in order to evaluate the stability of the modified membrane. The experimental conditions were the same as those used in Fig. 4.8. The feed solution contained 0.052 kg/m³ SDBS and 0.05M NaCl. The membrane was modified with 0.1 kg/m³ dopamine solution at pH 8.8 for 24 hours at 30 °C. Figure 4.12

shows the transition times (solid line) and the values of α corresponding to each membrane (broken lines) as a function of the period I kept membranes in Milli-Q water. Both transition time and α were decreased gradually with the time. The transition time for the unmodified membrane was zero for this feed solution as shown in Fig. 4.8. However, the transition time for modified membranes was still long even after three months of keeping in the water. In addition, the value of α was also still large compared with that for the unmodified membrane. Thus, it is clear that the membrane modified with PDA is very stable. This stability is probably because of the high adhesive force of PDA, which is regarded as a bio-glue [24].

In practical ED operation, electrolytes may affect the stability of the PDA coating. However, PDA particles have a negative charge and the PDA coating is a kind of fouling for AEM. The deposited PDA particles are always pressed against the membrane surface under the influence of applied DC voltage. Thus, the PDA layer will also be stable in practical ED operation.

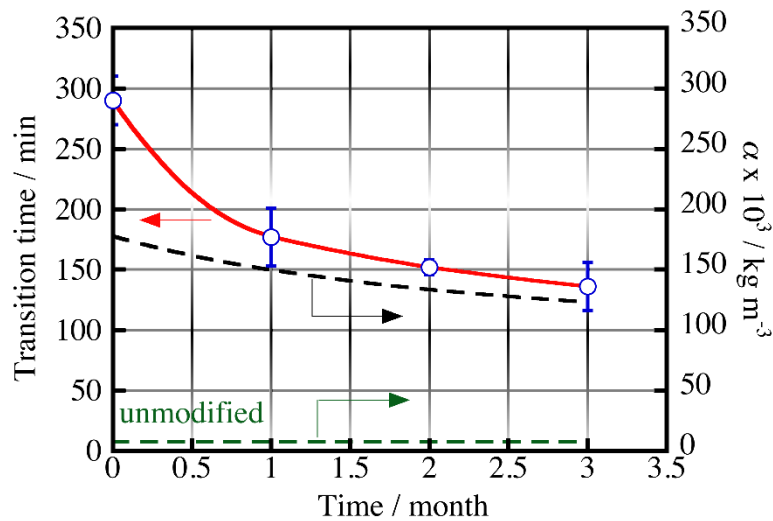


Fig. 4.12. Transition time and α as a function of period when the membrane was kept in Milli-Q water after modification.

4.4. Conclusion

Surface modification with PDA was attempted to improve the antifouling potential of anion exchange membrane in ED process. PDA has a strong adhesive force with many materials and it was expected to improve the negative surface charge and hydrophilicity of membrane. The membrane surface was modified by immersing the membrane in the dopamine solution at pH 8.8. The antifouling potential of AEM was evaluated with transition time, i.e. the time elapsed before fouling took place. The hydrophilicity of modified membrane surface increased with immersion time and became almost constant after 24 h immersion. The negative surface charge density and the hydrophilicity increased with increasing of dopamine concentration in the modification solution. On the other hand, the surface roughness increased with dopamine concentration. The increase in negative surface charge density and hydrophilicity indicates the increase of antifouling potential, while the increase in surface roughness indicates the decrease of antifouling potential. Improvement to overall antifouling potential was determined by the competition between improved antifouling potential through increasing in negative charge density and hydrophilicity of membrane surface and decreased antifouling potential through increasing in membrane surface roughness on the other. Consequently, the optimal dopamine concentration and optimum immersion time were 0.1 kg/m³ dopamine aqueous solution at pH 8.8 and 24 h, respectively. Under these conditions, the antifouling potential of anion exchange membrane was sufficiently improved.

In addition, the fouling data were analyzed theoretically with the model proposed. It was concluded that the adsorption of SDBS micelles were prevented by the surface modification with PDA through increased negative surface charge density and hydrophilicity. Furthermore, it was experimentally confirmed that the modified membrane was highly stable.

Nomenclature

C_{SDBS} : SDBS concentration of the feed (kg/m³)
 CMC : critical micelle concentration (kg/m³)
 E : electric field (V/m)
 M_s : membrane surface area (m²)
 t_{tran} : transition time (time elapsed before occurrence of fouling) (s)
 u : electrophoretic mobility of SDBS (m²/sV)
 α : concentration of SDBS above the CMC at which the fouling takes place (kg/m³)
 ΔE : voltage across the membrane (V)
 δ : thickness of the surface layer (m)

Abbreviations

AEM: anion exchange membrane
ED: electrodialysis
NF: nanofiltration
PDA: polydopamine
PVDF: poly(vinylidene fluoride)
RO: reverse osmosis
SDBS: sodium dodecylbenzene sulfonate

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Chapter 5

Effect of polydopamine coating and direct electric current application on anti-biofouling properties of anion exchange membranes in electrodialysis

5.1. Introduction

Global water shortage has become a critical problem because of the increasing global population, shrinking natural water resources, contamination of natural water sources and global warming [1, 2]. Membrane processes have attracted increasing attention as a promising method for water and wastewater treatment [3]. Membrane processes such as nanofiltration, reverse osmosis (RO) and electrodialysis (ED) are widely used to produce potable water from wastewater, brackish water, and seawater. ED is an electrochemical permselective separation process that uses cation and anion exchange membranes and has been applied to desalination and purification of brackish

water for more than half of century [4]. In the ED process, ions are selectively transported from one compartment (dilute) to another compartment (concentrate) through ion exchange membranes (IEMs) under applied potential difference as a driving force [4-6]. The most notable advantage of ED, comparing with other processes such as nanofiltration and RO, is a high water recovery because there is no osmotic pressure limitation. Moreover, ion exchange membranes have excellent durability because of their high mechanical and chemical stability. They can remove harmful monovalent anions such as F^- and NO_3^- , eliminate heavy metals and can soften water [6, 7]. However, despite these advantages, it is still necessary to improve monovalent anion permselectivity and to increase the fouling resistance of anion exchange membranes (AEMs) to improve ED performance.

Generally, AEMs have a higher selectivity for multivalent anions than monovalent anions, since AEMs have a positive charge. Then, the high selectivity for monovalent anions (relative to multivalent anions) is required to remove harmful anions such as NO_3^- and F^- to produce safe potable water with high current efficiency. In addition, if AEMs have a high multivalent anions selectivity, the concentration of multivalent anions such as SO_4^{2-} ion is increased too much in the concentrate compartment. It results in the precipitation of inorganic materials, known as “scaling”. The scaling is an inorganic fouling. Thus, the improvement in monovalent anion selectivity of AEMs is expected to decrease scale formation and consequently improves anti-inorganic fouling properties. In chapter 2, I showed theoretically that the monovalent anion permselectivity can be improved by surface modification of an AEM with a negatively charged layer [8]. Also in chapter 3, I verified this concept experimentally and showed

that the monovalent anion selectivity of the AEM was increased by polydopamine (PDA) coating because it formed a negatively charged layer on the membrane surface [9]. The negatively charged surface caused the Donnan exclusion of multivalent anions to become higher than that of monovalent anions, so that monovalent anion permselectivity was improved.

Membrane fouling, which leads to a decrease in membrane performance and an increase in running costs, is a complex issue affected by various parameters, alone and in combination [10, 11]. Membrane fouling is often classified by foulant substance. Foulants are classified into a non-living substance (organic fouling, inorganic fouling (scaling) and a living organism (biofouling (i.e., biofilm formation))). Membrane surface modification is very often applied to improve the fouling resistance of a membrane. In chapter 4, I reported that a PDA coating enhanced the anti-organic fouling performance of a commercial AEM by imparting high hydrophilicity and negative charge on the AEM surface [12]. As described above, mono-valent anion selectivity was improved by PDA coating of AEM surface. The improvement in monovalent anion selectivity of AEMs is expected to decrease scale formation and consequently improves anti-inorganic fouling properties [9]. Therefore, I have already improved monovalent anion permselectivity and anti-organic fouling property of an AEM for enhancing ED performance via PDA coating. The anti-inorganic fouling property is expected to be improved by PDA coating of AEM. Thus, the final remaining requirement for improving ED performance is to improve the anti-biofouling property.

Biofouling is the undesired attachment of microorganism communities to a membrane surface. Bacteria adhere on the membrane surface, grow and create a colony,

and consequently, the biofilm is formed. The biofouling is a very complex phenomenon and affected by the microorganism factors, membrane surface factors and feed water factors [13, 14]. The microorganism factors consist of species, cell number, surface charge and so on. The membrane surface factors consist of chemical composition, surface charge, hydrophilicity and so on. The feed water factors consist of temperature, pH, other dissolved substances and so on [15]. Many researches focus on biofouling in pressure driven membrane processes, such as RO [10, 14, 16]. On the other hand, few research on biofouling of ion exchange membranes is reported. Choi et al. reported the effect of biofouling on the proton transport and electric resistance of cation exchange membranes (CEMs) in a microbial fuel cell [17]. Pontié et al. attempted to improve an anti-biofouling property of CEMs by polyelectrolytes bilayer coating using layer-by-layer technique [18]. Most of the bacteria in water treatment processes are negatively charged [19]. Therefore, bacteria can easily adsorb on the AEM surface through electrostatic interactions with the fixed positive charges on the AEM. However, as far as we know, an anti-biofouling approach of anion exchange membrane is not reported.

The strategies to prevent biofouling are a prevention of a bacteria adhesion on membrane surface and a killing of bacteria. In the initial phase of the adhesion, it was reported that the behavior of killed and living bacteria were almost same [15]. It means the killed bacteria also adhere to the membrane surface. Thus, the most effective methods to prevent the biofouling is to prevent the bacteria adhesion on the membrane surface. Among membrane surface factors, it is widely accepted that a hydrophilic, negatively charged membrane surface is effective to prevent the bacteria adhesion and to improve anti-biofouling properties [20, 21]. Because PDA modification increases

hydrophilicity and negative charge density on the membrane surface, it is expected that a PDA coating will enhance the anti-adhesion properties (adhesion resistance of the membrane surface against bacterial attachment) of AEMs and consequently enhance the anti-biofouling properties of AEMs. Moreover, it was reported that a PDA coating on an RO membrane had slightly anti-bacterial properties and improved bacteriolysis via contact killing at pH 6 [22, 23]. Thus, in this chapter, I modified an AEM with a PDA coating, expecting that the coating would simultaneously improve all four ED process improvement requirements (monovalent anion permselectivity, anti-inorganic fouling, anti-organic fouling, and anti-biofouling). I also discuss the optimal conditions for PDA modification to improve total ED performance. The anti-biofouling property was generally evaluated by measuring the anti-adhesive properties. In addition, I investigated, for the first time, the biofouling behavior of an AEM during ED operation using a bacterial suspension as a feed solution. Finally, I studied the effect of applying a direct electric current (DC) on bacterial attachment and inactivation during ED operation.

5.2. Experimental

5.2.1. Materials

A NEOSEPTA AMX (Astom Corp., Tokyo, Japan) with strong basic anion exchange groups was used as the AEM. The characteristic properties of AMX were as follows: electric resistance 2.0×10^{-4} to $3.5 \times 10^{-4} \Omega \text{ m}^2$, and ion exchange capacity (IEC) 1.4–1.7 eq/kg dry membrane [7]. Dopamine hydrochloride (Sigma-Aldrich, Tokyo, Japan) was used to modify the AMX surface. NaCl and glutaraldehyde (Wako Pure Chemicals Industries, Ltd., Osaka, Japan) were necessary for a staining experiment and

used as an electrolyte and to fix the bacteria on the membrane surface, respectively. *Pseudomonas putida* (*P. putida*) (NBRC 100650) (Biological Resource Center at the National Institute of Technology and Evaluation, Shibuya, Japan) was used as a model Gram-negative bacterium because Gram-negative bacteria exist in water treatment processes [19]. Moreover, *P. putida* has a high adhesion property to the material surface [24]. A LIVE/DEAD BacLight Bacterial Viability kit (kit of SYTO 9 and propidium iodide (PI)) (Thermo Fisher Scientific, Waltham, MA, USA) was used to stain bacteria and Concanavalin A, Alexa Fluor 647 Conjugate (Thermo Fisher Scientific) was used to stain extracellular polymeric substances (EPS). The modified Fastidious Anaerobe Broth (FAB) medium was used for bacterial cultivation because it is suitable for biofilm formation of *Pseudomonas* species [25, 26]. The modified FAB medium consisted of 2.0 g/L glucose, 2 g/L (NH₄)₂SO₄, 4.7 g/L Na₂HPO₄, 3.0 g/L KH₂PO₄, 3.0 g/L NaCl, 11.0 mg/L CaCl₂, 95.0 mg/L MgCl₂, and 4.2 mg/L Fe (III)-EDTA. All solutions were sterilized by autoclave. Milli-Q water (18.2 MΩ·cm) (Millipore, Billerica, MA, USA) was used to prepare all solutions and for rinsing. All chemicals were used without further purification.

5.2.2. Membrane modification

AEM was modified with PDA, following reported methods in chapter 3 and 4 [9, 12]. Dopamine solution was prepared by dissolving a desired amount of dopamine in 15 mM Tris-HCl buffer aqueous solution (pH 8.8). The AMX membrane was immersed vertically in the freshly prepared dopamine solution, in contact with atmospheric oxygen, at 30°C for 24 h [12]. The dopamine concentration was varied (0.1 – 1.5 kg/m³)

for the experiments. After 24 h immersion, the membrane was removed from the dopamine solution and rinsed thoroughly with Milli-Q water for one day. The modified membranes were kept in Milli-Q water until required.

Dopamine spontaneously converts to PDA under alkaline condition, reacting with the oxygen of the air as shown in Fig. 5.1 and simultaneously adheres tightly to the AEM surface [27]. PDA is a bio-inspired polymer (i.e. a bio-glue) that is able to deposit non-selectively from solution onto any solid surface [28]. For the adsorption mechanism of PDA, both chemical and physical adsorption are reported [29]. In addition, PDA is very hydrophilic [30, 31]. PDA is an amphoteric substance with an isoelectric point around pH 4 [28, 32]. PDA forms a negatively charged layer on AMX membrane surfaces in a drinking water production process because the pH of drinking water is usually in the range 6.5 to 8.5 [33].

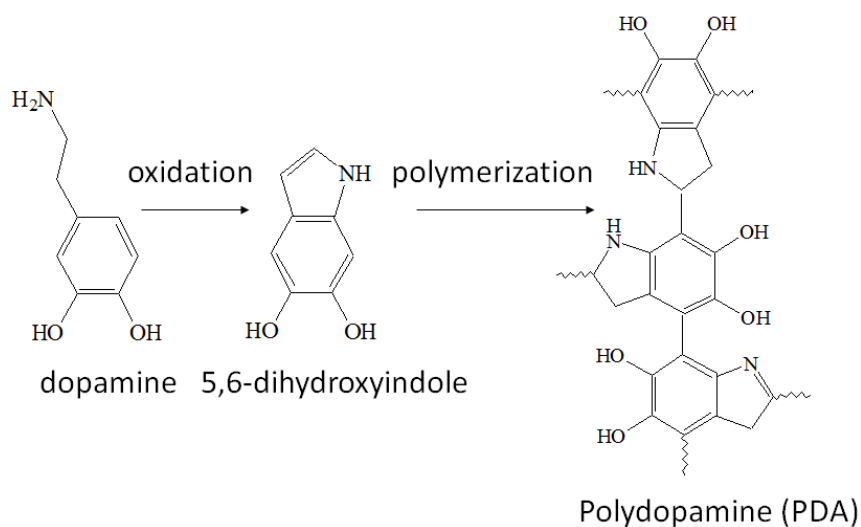


Fig. 5.1. Polydopamine formation [28, 34]

5.2.3. Scanning electron microscopy

The membranes were dried overnight in a freeze dryer (FDU-1200 EYELA; Tokyo Rikakikai Co. Ltd, Tokyo, Japan), and then coated with osmium tetroxide (OsO₄) prior to field emission scanning electron microscope (FE-SEM) measurements. A thin OsO₄ layer (about 5 nm) was formed using an osmium coater (Neoc-STB; MEIWAFOSS Co. Ltd, Tokyo, Japan). The membrane surfaces were observed using an FE-SEM (JSF-7500F; JEOL Co. Ltd, Tokyo, Japan) with an accelerating voltage of 7 kV.

5.2.4. Evaluation of anti-biofouling properties

5.2.4.1. Static adhesion test

The anti-adhesive properties of unmodified and modified AMX membranes were evaluated using a static adhesion test. In this test, *P. putida* was used as a model bacterium because of its high adhesive force and easy biofilm formation on membrane surface [19]. Figure 5.2 shows the timeline of the static adhesion test. *P. putida* was first inoculated into a modified FAB medium containing agar at a concentration of 15 kg/m^3 for 6 h at 30°C. *P. putida* was then precultured in the modified FAB medium for 18 h at 30°C. The precultured bacterial suspension was diluted 50 times with the modified FAB medium and cultured at 30°C for 4 h. Finally, the cultured bacterial suspension was diluted with modified FAB to an optical density (O.D.) of 0.05 at 450 nm (10^6 – 10^7

CFU/mL in bacteria concentration) and used for each experiment. The optical density was measured with a UV-VIS spectrophotometer (V-650, JASCO Corporation, Tokyo, Japan). This concentration of bacteria was much higher than that found in river water. For example, the amounts of bacteria in the Danube River (the second longest river in Europe) were investigated in 1988 and 2001 and reported as $4\text{--}5.3 \times 10^2$ and $6\text{--}7.5 \times 10^2$ CFU/mL, respectively [35]. The unmodified and modified membranes were immersed in 4 mL of *P. putida* suspension and incubated at 30°C for 18 h. The membranes were then taken out and immersed in a staining solution to stain the residual bacteria on each type of membrane surface for 20 min. The staining solution was prepared by mixing 3.3 µL of cell-permeable green fluorescence dye (SYTO 9), 3.3 µL of viable cell-impermeable red dye (propidium iodide (PI)), 200 µL of blue Concanavalin A (prepared by adding of 0.04205 g NaHCO₃ and 5 mL Milli-Q water to 5 mg Concanavalin A, Alexa Fluor 647 Conjugate) and 1800 µL of 0.85 wt% NaCl solution. The membranes were then dipped thoroughly into a mixed solution of 1800 µL of 0.85 wt% NaCl solution and 200 µL of 2.5% (v/v) glutaraldehyde solution to fix the adhered bacteria. After at least 10 min, the membrane surface was observed using Confocal Laser Scanning Microscopy (CLSM, FV 1000 D, Olympus Co. Ltd., Tokyo, Japan). For each sample, 10 different positions were observed by CLSM and analyzed using COMSTAT software. The average total cell volume ($\mu\text{m}^3/\mu\text{m}^2$) and the bacterial coverage (%) on the membrane surface were then calculated.

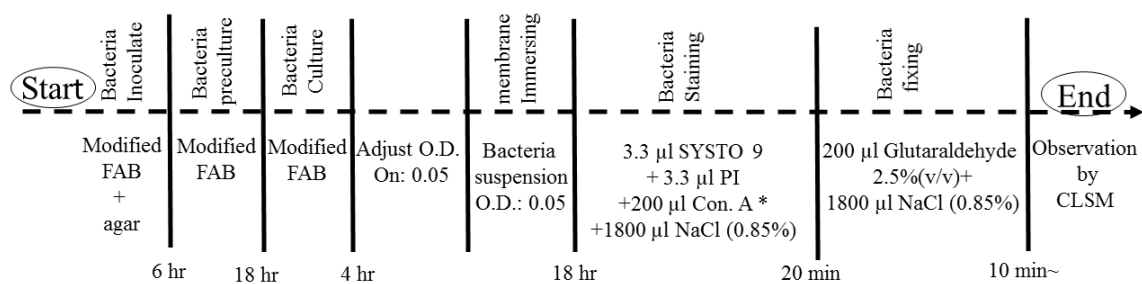


Fig. 5.2. Timeline of the static adhesion test.

*: Concanavalin A, Alexa Fluor 647 Conjugate

5.2.4.2. Anti-biofouling evaluation during ED operation

The anti-biofouling properties during ED process were evaluated using the same method as used for organic fouling [20, 21]. Figure 5.3 shows the experimental setup for measuring the fouling behavior. In the setup shown in Fig. 5.3, the left side corresponds to the dilute compartment and the right side to the concentrate compartment. The effective membrane area was $4 \times 10^{-4} \text{ m}^2$ ($0.02 \times 0.02 \text{ m}$), and the volume of each compartment was $1 \times 10^{-4} \text{ m}^3$. The feed solution was a *P. putida* suspension (O.D. 0.5) containing 0.05 M NaCl. It is notable that the O.D. in this experiment was 10 times higher than that used in an anti-adhesion test to accelerate biofouling. Then, in this experiment, the bacteria concentration was more than 10000 times higher than that found in river water [35]. The bacterial suspension was circulated from the reservoir through both compartments at a flow rate of $1.2 \times 10^{-3} \text{ m}^3/\text{min}$ at $30 \pm 1 \text{ }^\circ\text{C}$. Thus, the composition of the feed solution was held constant during the experiment. The applied DC density was constant at 20 A/m^2 , giving a total of 8 mA. This current density is lower than the limiting current density of AMX in 0.05M NaCl aqueous solution, about

70 A/m² [36]. The time course of the potential difference across the membrane, ΔE , during the biofouling experiment was measured with Ag-AgCl electrodes placed close to the membrane surfaces and was recorded with a data logger. The amount of DC used to form AgCl on Ag electrode was about twice of electric current transferred in each experiment. In addition, I reformed Ag/AgCl electrodes before each experiment. The electrode reaction during experiment is $\text{Ag} + \text{Cl}^- \leftrightarrow \text{AgCl} + \text{e}^-$. So, the pH of bulk solutions was not changed during experiment. In addition, the concentration of bacteria suspension (O.D.) was measured before and after the experiment to confirm the effect silver ions, since silver ions are known to have a bactericidal function. The value of O.D. increased a little after the experiment and it was confirmed that the effect of silver ions was negligible. This will be because the ion product of AgCl is extremely low and the concentration of silver ion was negligibly low.

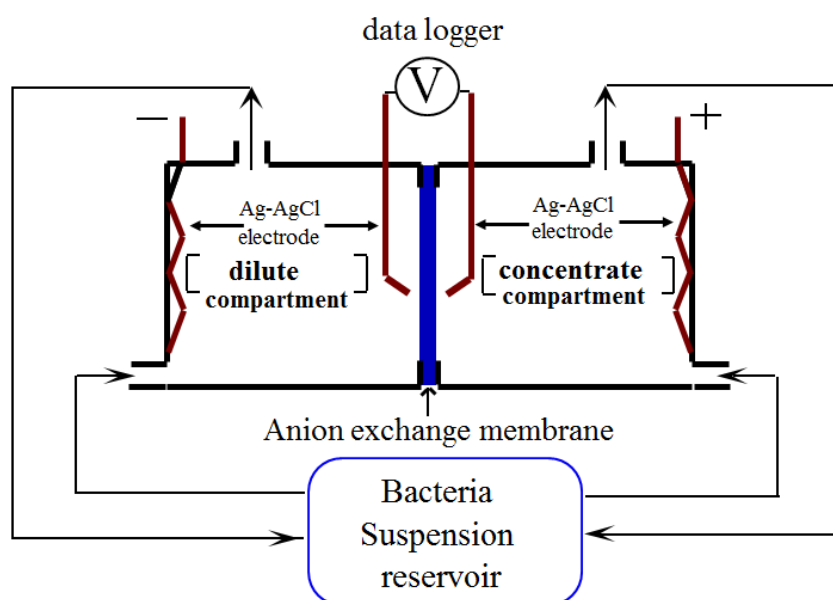


Fig. 5.3. Experimental setup for biofouling experiments.

The number of bacteria attached to the surface of the unmodified and PDA-modified membranes after the ED operation was observed using a field emission scanning electron microscope (FE-SEM) (JSF-7500F; JEOL Co. Ltd., Tokyo, Japan) with an accelerating voltage of 7 kV. After the experiment, the membranes were rinsed with 0.85 wt% NaCl solution and immersed in 2.5% (v/v) glutaraldehyde solution to fix the adhered bacteria for at least 10 min, then dried overnight in a freeze dryer and coated with osmium tetroxide (OsO₄) prior to FE-SEM measurements. A thin OsO₄ layer (ca. 5 nm) was formed using an osmium coater (Neoc-STB; MEIWAFOSSIS Co. Ltd., Tokyo, Japan). The surface observed by FE-SEM was analyzed using ImageJ software to calculate the bacterial coverage.

5.2.5. Surface roughness

The surface roughness of the unmodified and PDA-modified AMX membranes was measured by Color Laser Microscopy (KEYENCE Co., Vx-8510, Tokyo, Japan). The membranes were dried overnight in a freeze dryer and then the arithmetic average surface roughness, Ra was measured by scanning an area about 150 μm $\times$ 112 μm . The measuring resolution was 0.02 μm . The measured Ra may become a little smaller than the Ra under a wetting condition by shrinking due to the freeze dry. But, it will be enough to discuss the effect of surface roughness on biofouling. The measured roughness corresponds to the roughness of SEM images shown in Fig.5.4.

5.3. Results and discussion

5.3.1. Modified membrane surface

The SEM images of the membrane surface were taken to study the morphology changes of the membrane surface caused by PDA modification. Figure 5.4 shows the SEM images of unmodified and modified AMX membranes [12]. It is found that the particle size of PDA deposited on the membrane surface increased with increasing dopamine concentration. The surface of PDA-modified AMX was uniform and smooth up to 0.1 kg/m^2 (Fig.5.4 (b)). The particle size of PDA shown in Fig.5.4 (b) is the order in nm. This particle size is consistent with that reported in other study [15]. The PDA particles aggregated on the membrane surface when the dopamine concentration exceeded 1 kg/m^3 . It is clear from Fig.5.4 that the morphology of membrane surface changed depending on the dopamine concentration used to modify membrane. It was expected that the change of surface morphology resulted in the change of roughness of the membrane surface. This is discussed further in Section 5.3.3 combined with the roughness data because it is known that roughness strongly influences antifouling properties [37].

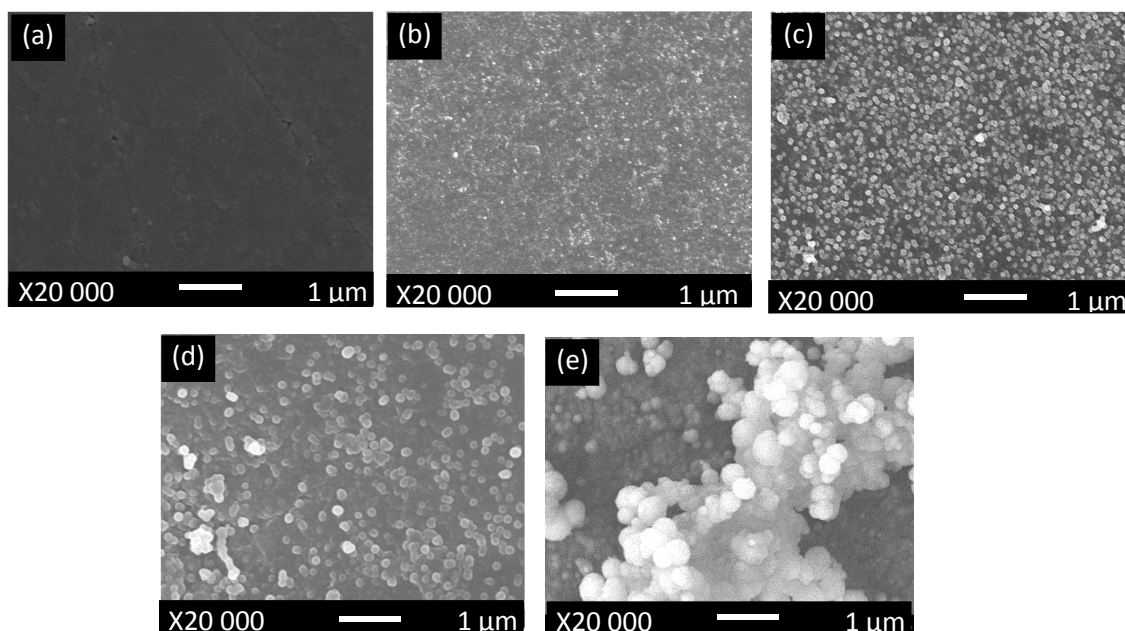


Fig. 5.4. FE-SEM images of membrane surfaces modified with (a) 0 kg/m³ (unmodified membrane), (b) 0.1 kg/m³, (c) 0.5 kg/m³, (d) 1 kg/m³ and (e) 1.5 kg/m³ dopamine solution [12].

5.3.2. Static adhesion test

Figure 5.5 shows the unmodified and PDA-modified AMX membrane surfaces observed by CLSM after 18 h immersion in a *P. putida* bacterial suspension.

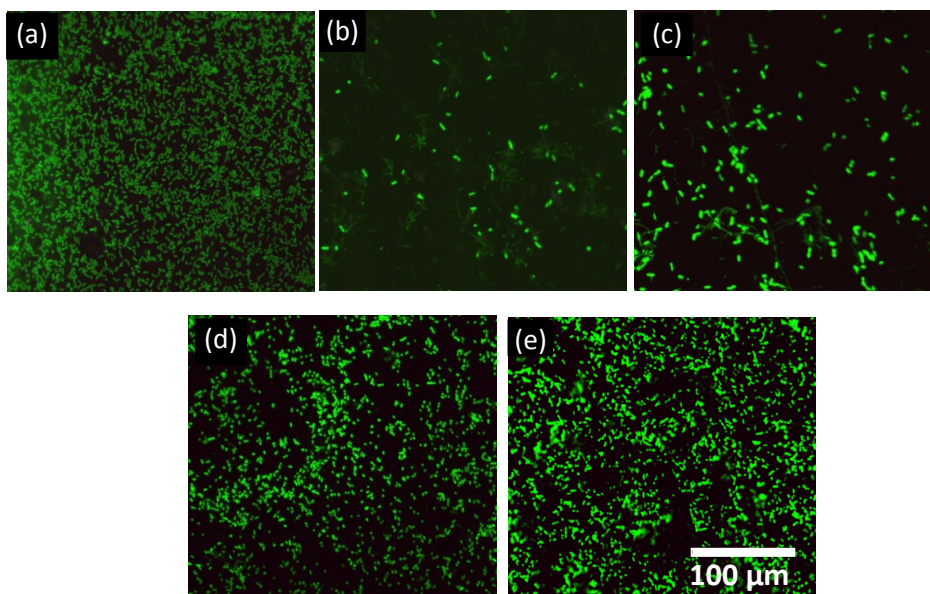


Fig. 5.5. CLSM images of (a) unmodified AMX membrane surface, (b) AMX membrane surface modified with 0.1 kg/m^3 , (c) 0.5 kg/m^3 , (d) 1 kg/m^3 , and (e) 1.5 kg/m^3 dopamine. The black background is the membrane surface and green points are stained viable bacteria.

In Fig. 5.5, the black background shows the membrane surface and the green points are stained, live bacteria. No dead bacteria were found on any membrane surface, because red spots were not observed in any CLSM images. The EPS formation was also insignificant. It is clear from Fig. 5.5 that the number of bacteria adsorbed on the membrane surface was decreased by PDA coating (b) and then increased with dopamine concentration (c–e).

The colony heights on the membrane surface were obtained by analyzing the CLSM images with COMSTAT software and are shown in Fig. 5.6. In Fig. 5.6, the blue background shows the membrane surface and the spots show stained, live bacteria. The color intensity of the spots depended on the height of the attached bacterial colony. The

total cell volumes and coverage were obtained from Fig. 5.6 using COMSTAT software and are shown in Fig. 5.7 (a) and (b), as a function of dopamine concentration, respectively. It was found in Fig. 5.7 that the total cell volumes attached on the AEM surface (Fig. 5.7 (a)) and bacterial coverage (Fig. 5.7 (b)) decreased with increasing dopamine concentration in the modification solution, and then increased after showing a minimum at around 0.1 kg/m^3 dopamine modification concentration. These values were lower than that for the unmodified membrane (at zero on the x-axis), even for the 1.5 kg/m^3 dopamine modification case. It is clear that the attachment and growth of bacteria on the membrane surface was effectively suppressed by PDA coating. The bacterial attachment was suppressed through increased hydrophilicity and the presence of negative surface charges on the membrane surface as shown in Fig. 5.8 [12].

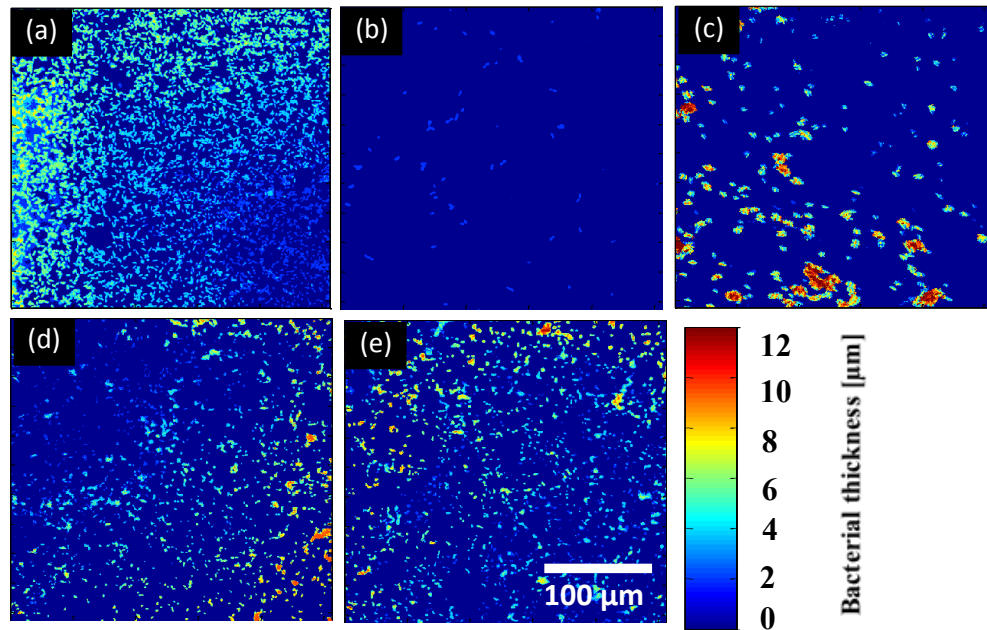


Fig. 5.6. Analyzed CLSM images of (a) unmodified AMX membrane surface, (b) AMX membrane surface modified with 0.1 kg/m^3 , (c) 0.5 kg/m^3 , (d) 1 kg/m^3 , and (e) 1.5 kg/m^3 dopamine. The blue background is the membrane surface and yellow spots are stained viable cells.

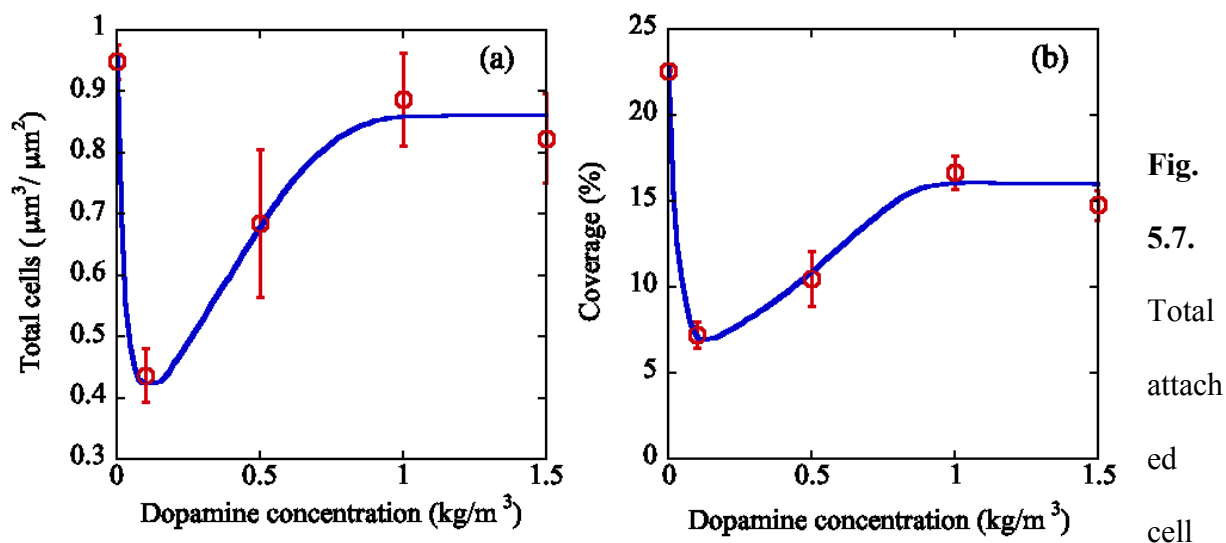


Fig. 5.7. Total attached cell volume (a) and coverage percentage (b) on the AMX membrane surface as a function of dopamine concentration.

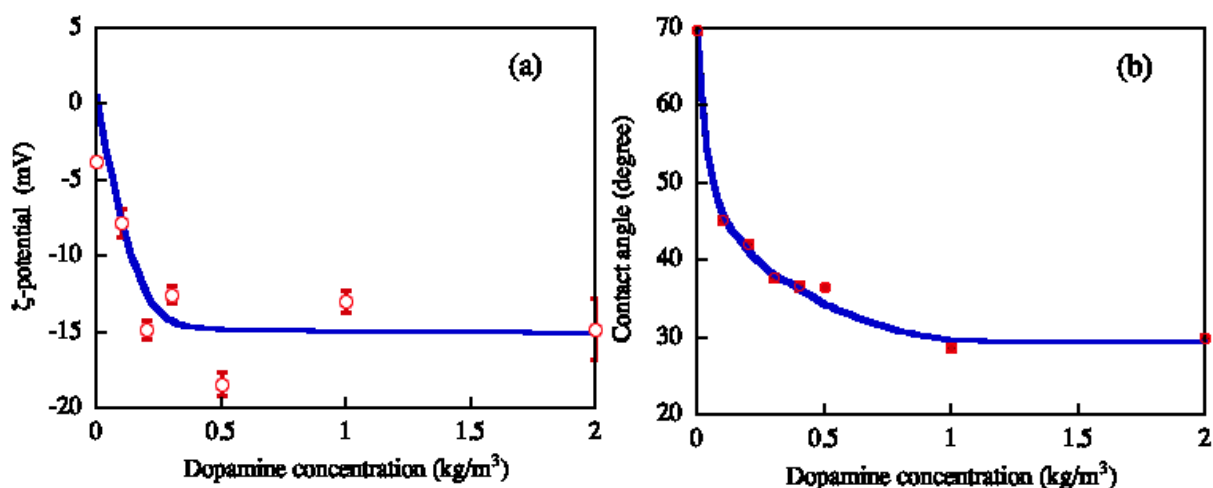


Fig. 5.8. ζ -potential and contact angle of modified AMX as a function of dopamine concentration [12].

5.3.3. Surface roughness evaluation

As shown in Fig. 5.8, the hydrophilicity and the negative charge density increased with the dopamine concentration in the modification solution [12]. Nevertheless, as shown in Fig. 5.7, the bacteria volume and coverage on the membrane surface increased with increasing dopamine concentrations above 0.1 kg/m^3 . This tendency may be

attributed to surface morphology change. As shown in Fig. 5.4, the surface of the PDA-modified membrane was uniform and smooth up to 0.1 kg/m³ dopamine and then the PDA particle size increased and aggregates were formed on the membrane surface. Surface roughness affects fouling resistance [37], so the increase in bacteria volume and coverage above 0.1 kg/m³ dopamine may have been caused by an increase in surface roughness. Therefore, the roughness of the AMX surface was measured as a function of dopamine concentration to confirm this expectation.

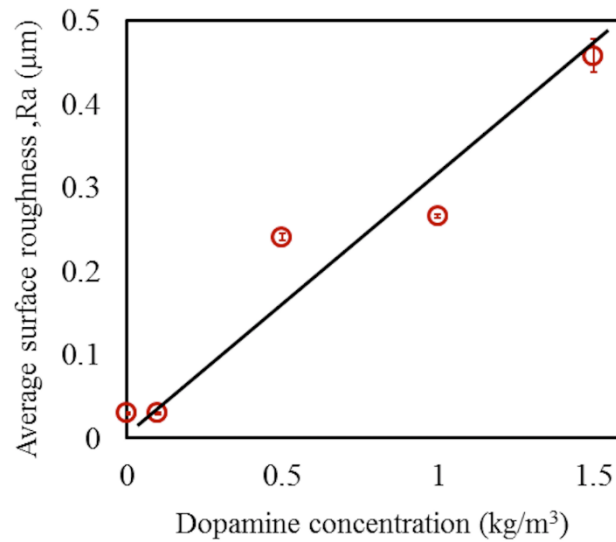


Fig. 5.9. Arithmetic average surface roughness of unmodified and modified AMX membranes as a function of dopamine concentration.

Figure 5.9 shows the arithmetic average surface roughness, R_a of the modified AMX membrane measured with Color Laser Microscopy, as a function of dopamine concentration. The value at 0 kg/m³ dopamine corresponds to the unmodified AMX. It was found that the surface roughness of unmodified and modified (0.1 kg/m³ dopamine) membranes were the same within the measurement resolution of 0.02 µm. This is reasonable since the PDA particle size deposited on AMX membrane modified by 0.1

kg/m³ dopamine is smaller than 0.02 μm as shown in Fig. 5.4(b). Then, I could not detect the increase of roughness due to PDA particle deposited on AMX surface. On the contrary, the surface roughness significantly increased with dopamine concentration above 0.1 kg/m³. The roughness for the AMX modified by 0.5 and 1 kg/m³ of dopamine was almost same whereas the total attached cell volume and coverage percentage were significantly higher at 1 kg/m³ as shown in Fig.5.7. This is because the roughness shown in Fig. 5.9 is the roughness of z-axis (perpendicular to surface). On the other hand, it is clear from SEM images shown in Fig. 5.4 that the PDA particle size on AMX membrane surface modified by 1 kg/m³ of dopamine is larger than that on AMX membrane surface modified by 0.5 kg/m³ of dopamine. This difference in particle size resulted in the difference in morphology, even though the roughness on z-axis is the same. This difference in morphology resulted in the difference in the total attached cell volume and coverage percentage.

Thus, it was concluded that 0.1 kg/m³ dopamine modification was the optimal concentration to improve anti-biofouling properties, because the hydrophilicity and negative charges on the AMX surface were effectively increased as shown in Fig. 5.8 [12], while the AMX surface roughness was negligibly increased.

5.3.4. Anti-biofouling evaluation under ED operation

To investigate the biofouling behavior of AEM during ED operation, I measured the biofouling properties of unmodified and the PDA-modified AMX membranes during ED operation, using a *P. putida* suspension as a feed solution, as described in Section 5.2.4.1. The *P. putida* suspension (O.D.₄₅₀: 0.5) contained 0.05 M NaCl and the

concentration of cells used in this experiment was ten times higher than that used in the anti-adhesion test to accelerate biofouling during the ED process, whereas the applied bacteria concentration used in the anti-adhesion test was also far higher than that of river water.

Figure 5.10 shows an example of experimental data for the time course of potential difference across the membrane, ΔE [12]. At first, the foulant is carried to the membrane surface by electrophoretic migration and the foulant concentration in a thin surface region close to the membrane surface increases. This results in the gradual increase of potential difference across the membrane. While the foulant concentration in the thin surface region is low, the electrostatic repulsion of between the negative charge of foulant and the negative charge of membrane surface prevented the foulant to adsorb onto the membrane surface. However, this repulsive force becomes weaker and weaker with the increase of foulant concentration in the thin surface region. When this foulant concentration exceeds a critical concentration, the foulant starts to adsorb onto the membrane surface and ΔE starts to increase drastically as shown in Fig. 5.10. This is the start of fouling. The time elapsed until the fouling occurs is called the transition time, t_{tran} . The transition time is long when little fouling takes place but it is short when fouling occurs readily. Thus, the transition time was used as a suitable parameter that reflects the anti-fouling potential of the AEM.

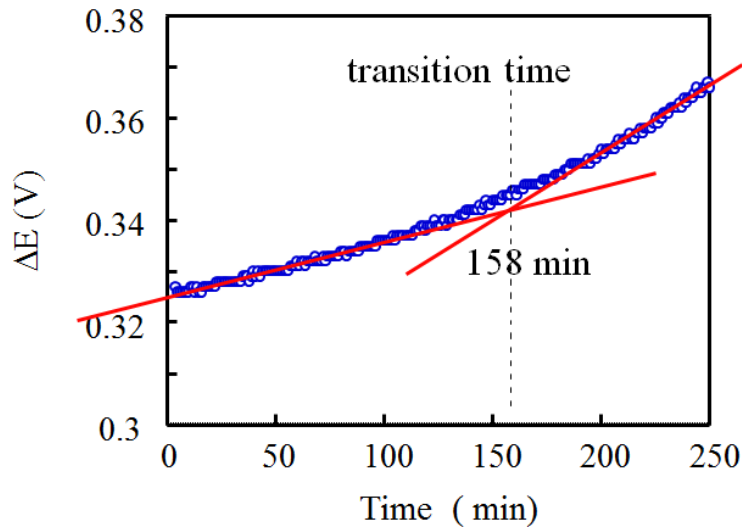


Fig. 5.10. The potential difference across the membrane and the determination of transition time. The feed solution (pH 6.2) contained 0.05 M NaCl as an electrolyte and 0.052 kg/m³ sodium dodecylbenzene sulfonate (SDBS) as a foulant. The membrane was modified with 0.05 kg/m³ dopamine solution at pH 8.8 for 24 h [12].

Figure 5.11 shows the time course of ΔE in biofouling experiment for the AMX membrane modified with 1 kg/m³ dopamine solution. The data for other membranes including unmodified membrane were the same as Fig. 5.11. It is clear that ΔE did not increase with time and remained almost constant, meaning that fouling did not take place. When fouling occurs, ΔE should increase through an increase in the electrical resistance of the membrane under a constant electric current, as shown in Fig. 5.10. However, ΔE was almost constant during this experiment. It can be concluded that biofouling scarcely occurred during practical ED operation. Because, biofouling did not take place even in the presence of a high concentration of bacteria in the feed solution. It is expected that biofouling will not be a serious problem in practice, especially when the ED process is applied for river waters to make a drinking water. Because, the

bacterial concentration in river waters is much lower than that of the bacterial concentration used in this study, as described above.

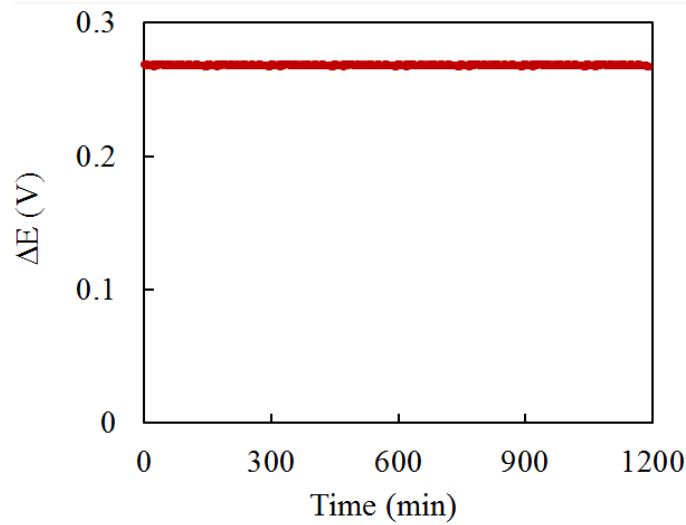


Fig. 5.11. An example of the potential difference across the membrane used to determine the transition time. AMX was modified with 1 kg/m³ dopamine, Current density: 20 A/m² (8 mA), Bacterial suspension: (O.D.₄₅₀: 0.5), Temperature: 30°C.

However, if the electric resistance of biofouling layer on the AMX surface is negligibly small, ΔE will not change even if the biofouling takes place. It is reported that a biofouling does not increase a membrane resistance so much [17]. Then, as a further investigation, the membranes were removed after biofouling experiments and their surfaces were observed by FE-SEM to evaluate the effect of the PDA coating on the anti-adhesive properties of AMX surface during ED operation. Figure 5.12 shows FE-SEM images of unmodified AMX and AMX modified with differing dopamine concentrations, after 1200 min of the biofouling experiment under ED operation. It can be seen that the number of bacteria attached on the membrane surface was markedly

decreased by PDA modification with a 0.1 kg/m^3 dopamine solution. The FE-SEM images were analyzed using ImageJ software to obtain the surface coverage by bacteria.

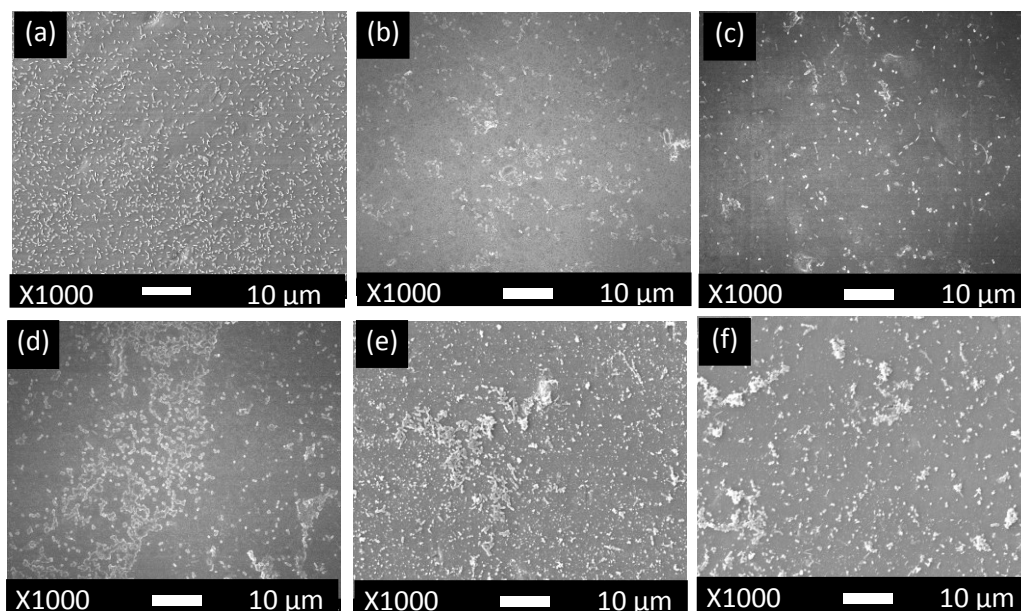


Fig. 5.12. FE-SEM images of (a) unmodified AMX membrane surface, (b) AMX modified with 0.1 kg/m^3 , (c) 0.2 kg/m^3 , (d) 0.5 kg/m^3 , (e) 1 kg/m^3 , and (f) 1.5 kg/m^3 dopamine after 20-h biofouling experiments under ED operation.

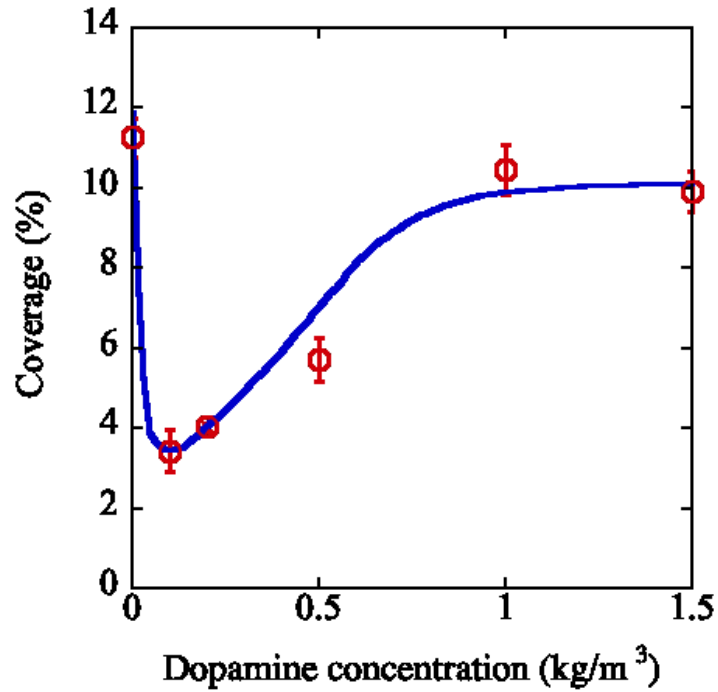


Fig. 5.13. Surface coverage on unmodified and modified AMX membranes as a function of dopamine concentration after 20-h biofouling experiments under ED operation.

Figure 5.13 shows the surface coverage by bacteria during ED operation as a function of dopamine concentration. Figure 5.13 shows a tendency identical to Fig. 5.7 (b), with a minimum at 0.1 kg/m³ dopamine modification. However, the surface coverage in Fig. 5.13 is lower than that of Fig. 5.7 (b), even though the bacteria concentration in Fig. 5.13 was 10 times higher than that used in Fig. 5.7 (b) and the operation time was 2 h longer. Moreover, the surface coverage for the unmodified membrane (0 on the x-axis) in Fig. 5.13 was about 11.5%, which was lower than that in

Fig. 5.7(b) (about 22.5%). This probably indicates that DC application reduced the bacterial attachment. However, it is not clear which is dominant for this phenomenon, DC electric field or the electric current at this point.

Figure 5.14 (a) shows the membrane surface after immersion in the bacterial suspension (O.D.₄₅₀: 0.05) for 18 h with no applied electric current, while Fig. 5.14 (b) shows the membrane surface after 20 h ED operation using the bacterial suspension (O.D.₄₅₀: 0.5) as a feed solution. It was found from Fig. 5.14 that the shape of *P. putida* changed during ED operation, in addition to the decrease in the number of the attached bacteria. These phenomena are consistent with previous reports. Liu et al. showed that current application influenced the number and growth of bacteria over a long period (e.g. 24 h) [38]. In addition, Luo et. al. reported that the electric current caused significant changes in the surface properties and shape of cells [39]. Therefore, it was concluded that the electric current application effectively improved the anti-biofouling performance during the ED process.

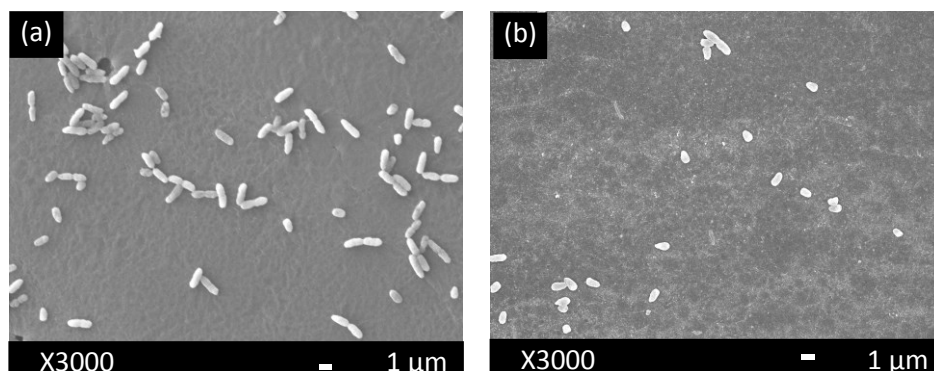


Fig. 5.14. FE-SEM images of AMX modified with 0.1 kg/m³ dopamine (a) after immersing in a *P. putida* bacteria suspension with O.D.₄₅₀: 0.05 for 18 h and (b) after 20h biofouling experiments under ED operation with a *P. putida* bacterial suspension (O.D.₄₅₀: 0.5) under a constant current of 20 A/m².

5.3.5 Improvement of total ED performance

In this section, I discuss the effect of PDA coating on a total performance of ED system by discussing the data on biofouling combined with the data on organic fouling and monovalent anion selectivity previously reported. In Fig. 5.15 (a), the dashed line shows the transition time previously measured with sodium dodecylbenzene sulfonate (SDBS) as an organic foulant [12]. The solid line shows the surface coverage by bacteria during the ED process obtained in this study. A long transition time means a higher anti-fouling property. This figure gives us a proper comparison between anti-organic fouling and anti-biofouling property tendencies as a function of dopamine concentration. It was found that the optimal concentration for improving both anti-organic fouling and anti-biofouling was the same, at 0.1 kg/m³.

Figure 5.15 (b) shows the transport number ratio between SO_4^{2-} and Cl^- , $P^{\text{SO}_4}_{\text{Cl}}$ of AMX as a function of dopamine concentration [9]. In Fig. 5.15 (b), a $P^{\text{SO}_4}_{\text{Cl}}$ value higher than unity indicates that the divalent anion selectivity of AMX was higher than its monovalent anion selectivity and a $P^{\text{SO}_4}_{\text{Cl}}$ value lower than unity indicates that the monovalent anion selectivity is higher than the divalent anion selectivity. Thus, because $P^{\text{SO}_4}_{\text{Cl}}$ was about 0.6, it was found that

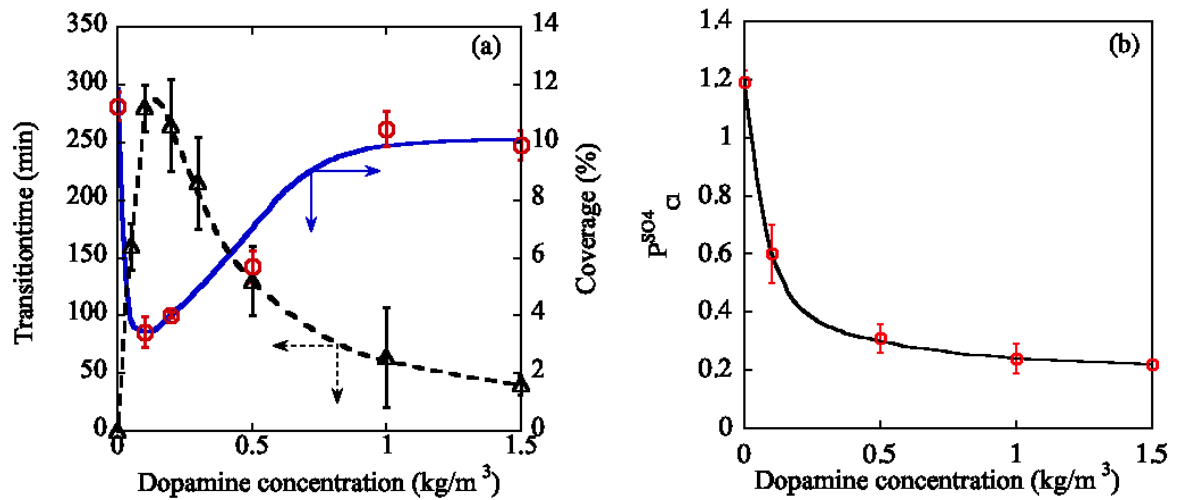


Fig. 5.15. The transition time (dashed line) and coverage (solid line) (a) and monovalent anion permselectivity between SO_4^{2-} and Cl^- (b) as a function of dopamine concentration.

Therefore, it is clear that the antifouling properties, including biofouling and organic fouling, and the monovalent anion permselectivity of the ED system were effectively and simultaneously improved by surface modification of AEM with PDA at an optimal concentration of 0.1 kg/m³ dopamine solution. Improvement in monovalent anion selectivity is expected to decrease scale formation and consequently improves anti-inorganic fouling properties. Consequently, the overall performance of the ED system was improved by surface modification of AEM.

5.4. Conclusion

The effect of PDA coating of an AMX membrane surface on biofouling was evaluated using a static adhesion test and the transition time during ED operation. In the adhesion test, the total cell volume and coverage were determined by analyzing CLSM images using COMSTAT software. The total cell volume and coverage of PDA-modified membranes decreased with dopamine concentration used during modification and then increased after showing a minimum at 0.1 kg/m³ dopamine. The increase in total cell volume and coverage with dopamine concentration after the minimum point was attributed to an increase in modified surface roughness.

For the measurement of transition time during ED operation, the experiment was carried out using a bacterial suspension as a feed solution. The potential difference across the membranes during ED operation did not increase, even for unmodified membrane, even though an extremely high bacteria concentration was used relative to that in real river water. Furthermore, the membrane surfaces were observed by FE-SEM and analyzed using ImageJ software to obtain the coverage after biofouling experiments

during ED operation. The coverage on the membrane surface showed the same tendency as the static adhesion test, giving a minimum at 0.1 kg/m^3 dopamine. However, the minimum value during ED operation was lower than that found in the adhesion test, even though the bacterial concentration was 10 times higher than that used in the adhesion test. In addition, it was found by SEM observation of fouled membrane surfaces that the shape of the bacterial cells changed during ED operation. This indicates that DC application inhibits bacterial attachment to the AEM surface and that biofouling may scarcely occur during a real ED operation.

Considering all of the results, including those reported in chapters 3 and 4, it is concluded that 0.1 kg/m^3 is the optimal concentration of dopamine for membrane modification to improve overall ED performance. Because, the surface modification with 0.1 kg/m^3 dopamine solution simultaneously improved anti-biofouling, anti-organic fouling, and monovalent anion permselectivity. Improvement in monovalent anion selectivity is expected to decrease scale formation and consequently improves anti-inorganic fouling properties.

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Chapter 6

Biofouling Phenomena on Anion Exchange Membrane Under Reverse electrodialysis Process

6.1. Introduction

Energy generation from nonpolluting sustainable energy sources such as blue energy has drawn significant attention because of the depletion of fossil fuel sources, rising CO₂ emissions, and increased pollution. For instance, energy can be provided using untapped and renewable water sources including oceans, seas, and surface waters. Mixing two water streams with different salt concentrations (e.g., seawater and river water) through membranes generates salinity gradient energy (SGE). Although the energy generated by the salinity gradient is very low in comparison with the energy produced by fossil fuels, SGE is clean, nonpolluting, and sustainable. SGE is also the second largest marine-based energy source, with an estimated global potential of 2.4–

2.6 TW [1-4], and can therefore play an important role in providing the energy required in the future.

Reverse electrodialysis (RED) is a membrane-based electrochemical process and a dialytic battery. The stack design of RED is essentially same as that of an electrodialysis (ED) process. In RED, the cells (containing an anion exchange membrane (AEM) and a cation exchange membrane (CEM), as well as low and high salinity water compartments) are arranged alternately between two electrodes. However, the input and output are the opposite of those used in ED, where the input is an electric current and the outputs are low and high salinity waters. On the other hand, in RED, the inputs are low and high salinity waters and the output is an electric current shows a schematic of an RED system. Electric power is obtainable when the membrane stack potential

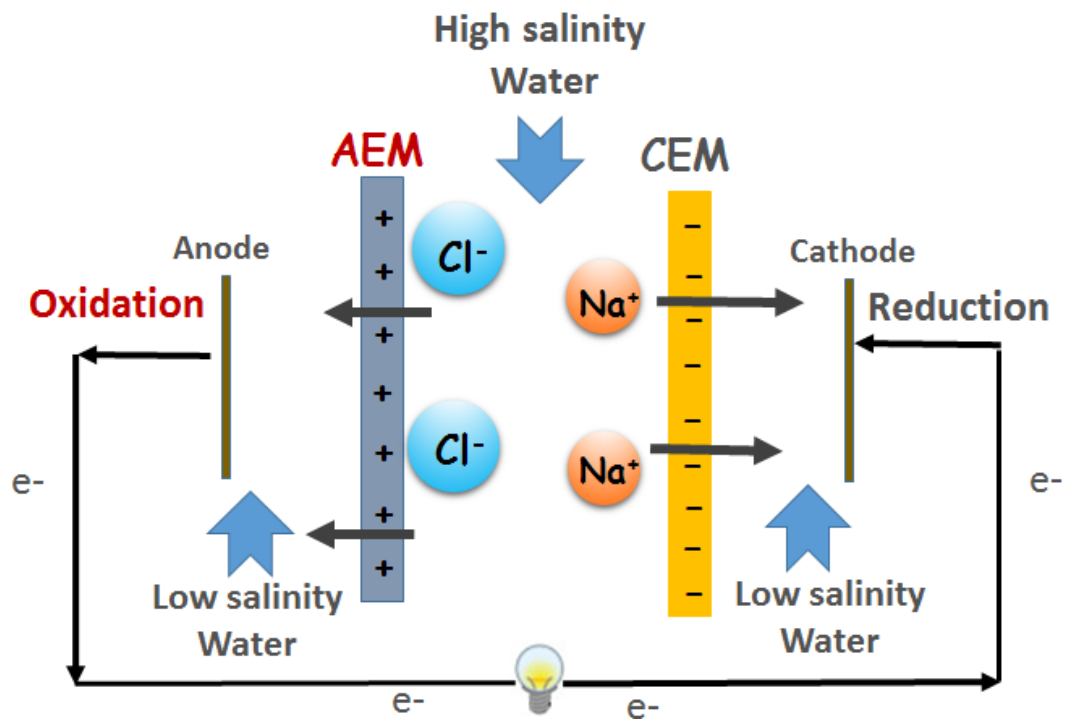


Fig. 6.1. Schematic of RED principle

exceeds the redox potential at the electrodes, causing a current to be generated [5, 6]. Anions migrate to the anode through the AEM and cations migrate to cathode through the CEM under electrochemical potential gradients. The ionic current is converted into electric current by the redox reactions at the electrodes.

As with other membrane technology processes, fouling is an issue in RED, and presents a further obstacle besides low power density and high cost that has hindered the commercialization of the RED process and its large-scale application [7,8]. Fouling includes organic fouling, inorganic fouling, and biofouling, all of which influence the ion exchange membranes (IEMs) and consequently reduce RED performance. In RED systems, AEMs (containing positive fixed charges) are most likely to be affected by organic fouling and biofouling, while CEMs (containing negative fixed charges) are more prone to inorganic fouling (scaling) [7]. Biofouling of AEMs in particular is a severe problem in RED, since a practical application of a RED system would plan to use natural seawater and river water to generate energy.

Ratjke et al. evaluated the effect of fouling on the power output of RED [9]. When using natural seawater and artificial river water, they found that the power density decreased by 67% due to biofouling. Vermaas et al. investigated fouling behavior in RED when using natural seawater and river water. Several strategies were proposed to improve anti-fouling properties, such as using profiled membranes (i.e., spacerless stacks) [7]. The same group reported that the power density sharply decreased in the first few hours of operation when anti-fouling strategies were not applied in the process. They then showed that using periodic feed water reversal (i.e., switching seawater with

river water and vice versa) and air sparging as anti-fouling approaches significantly improved the performance of RED systems [10]. The aforementioned studies tried to improve anti-fouling properties by optimizing operational conditions and modifying the stack design. However, they did not take into account the membrane properties, even though IEMs were the heart of the RED system.

The introduction of a negatively charged polyanion layer on AEMs through surface modification is a promising method of improving anti-fouling properties. Our previous studies showed that the increase in surface hydrophilicity and negative surface charge density sufficiently increased fouling resistances (including resistance to biofouling) of AEMs [11-13]. In addition, I showed that the surface hydrophilicities and negatively charged densities of AEMs were notably enhanced by a polydopamine (PDA) coating. I sufficiently improved the anti-organic fouling and anti-biofouling of an AEM under ED operation [13,14]. Thus, these results encouraged me to use the same modification method to study the biofouling behavior of AEMs during RED. To the best of my knowledge, no work has been reported on attempts to improve the anti-biofouling performance of AEMs under RED operation through surface modification. In this study, I investigated the biofouling behavior of AEMs during RED for the first time. The bacteria *Pseudomonas putida* (*P. putida*) was used as a model biofoulant, and I modified a commercial AEM with the optimal concentration of polydopamine [13]. Biofouling on unmodified and modified AEMs was then evaluated by measuring bacterial coverage percentage (i.e., biofouling formation) using scanning electron microscopy (SEM) images. In addition, the effects of electric field and electric current during RED on bacterial attachment and shape are discussed.

6.2. Experimental

6.2.1. Materials

A NEOSEPTA AMX membrane (Astom Corp., Tokyo, Japan), which has strongly basic anion exchange groups, and a NEOSEPTA CMX membrane (Astom Corp.) were used as AEMs and CEMs, respectively. The physical properties of AMX and CMX are listed in Table 6.1 [15] .

Table 6.1 Physical properties of CMX and AMX.

Membrane	Structure properties	IEC (meq/g dry-membrane)	Thickness (mm)	Water Content (%)	Area Resistance* ($\Omega \text{ cm}^2$)	Permselectivity** (%)
Neosepta CMX	Cation, PS/DVB	1.5-1.8	0.14-0.20	25-30	1.8-3.8	97
Neosepta AMX	Anion, PS/DVB	1.4-1.7	0.12-0.18	25-30	2.0-3.5	95

PS: Polystyrene; DVB: Divinyl benzene; *: 0.5 M NaCl and **: 0.1/0.001 M NaCl at 25 °C.

Dopamine hydrochloride (Sigma-Aldrich, Tokyo, Japan) was used to modify the AMX surface. NaCl and glutaraldehyde (Wako Pure Chemicals Industries, Ltd., Osaka, Japan) were used as the electrolyte and to fix the bacteria on the membrane surface, respectively. $\text{K}_4\text{Fe}(\text{CN})_6$, and $\text{K}_3\text{Fe}(\text{CN})_6$, (Wako Pure Chemicals Industries, Ltd., Japan) were used to make an electrode rinse solution.

Pseudomonas putida (*P. putida*) (NBRC 100650) (Biological Resource Center at the National Institute of Technology and Evaluation, Shibuya, Japan) was used as a

model Gram-negative bacterium, because of its high adhesion to the material surface [16]. A modified Fastidious Anaerobe Broth (FAB) medium was used for bacterial cultivation, as it is suitable for formation of biofilms of *P. putida* [17,18]. The modified FAB medium consisted of 2.0 g/L of glucose, 2 g/L of $(\text{NH}_4)_2\text{SO}_4$, 4.7 g/L of Na_2HPO_4 , 3.0 g/L of KH_2PO_4 , 3.0 g/L of NaCl , 11.0 mg/L of CaCl_2 , 95.0 mg/L of MgCl_2 , and 4.2 mg/L of Fe(III)-EDTA. All solutions were sterilized by autoclave. Milli-Q water (18.2 M Ω /cm) (Millipore, Billerica, MA, USA) was used to prepare all solutions and for rinsing. All chemicals were used without further purification.

6.2.2. Membrane modification

AEM was modified with PDA following previously reported methods [13,16]. Dopamine solution was prepared by dissolving 0.1 kg/m³ of dopamine in 15 mM Tris-HCl aqueous buffer solution (pH 8.8). The AMX membrane was vertically immersed in the freshly prepared dopamine solution, in contact with atmospheric oxygen, at 30 °C for 24 h [13]. After 24 hours immersion, the membrane was removed from the dopamine solution and rinsed thoroughly with Milli-Q water for one day. The modified membranes were kept in Milli-Q water until required.

Dopamine spontaneously converts to PDA under alkaline condition by reacting with oxygen in the air as shown in Fig. 6.2, and simultaneously adheres tightly to the AEM surface [19]. PDA is a bio-glue that is very hydrophilic and able to deposit non-selectively from solution onto any solid surface [19-22].

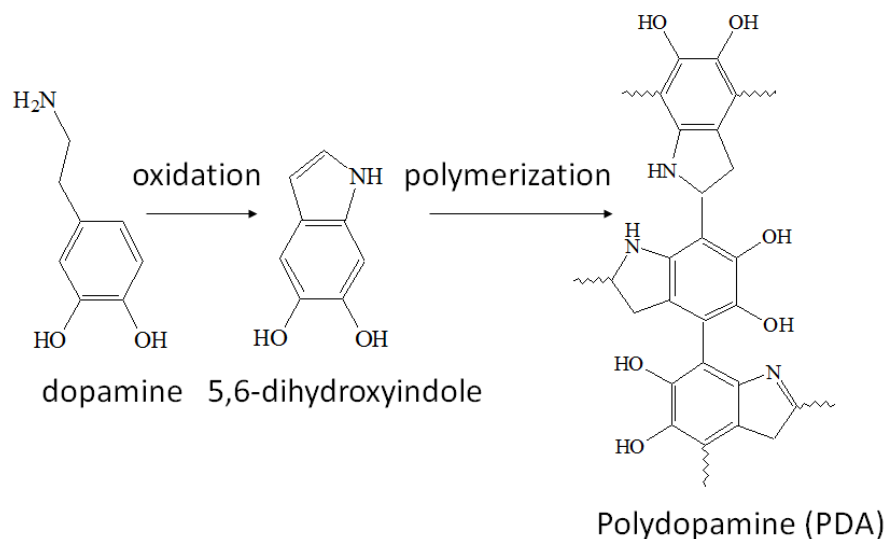


Fig. 6.2. Polydopamine formation [20, 23].

6.2.3. RED stack

A schematic of a RED stack is shown in Fig.6.3 AMX and CMX were placed between two endplates. Each endplate was made from poly(methylmethacrylate) (PMMA) equipped with titanium mesh electrodes coated with iridium and rubidium (4.5×4.5 cm) as the anode and cathode. The effective membrane surface area was 20.25 cm^2 (4.5×4.5 cm). A gasket with a thickness of $300 \text{ }\mu\text{m}$ was inserted between each membrane pair to create low and high salinity compartments. An additional CMX was placed at the end of stack as a shielding membrane to prevent leakage of the electrode rinse solution towards the inside of stack and vice versa. A solution containing NaCl

through the stack at a flow rate of 300 mL/min. Two types of high salinity water were prepared: a) an aqueous solution of NaCl (0.507 M) was used in control experiments, and b) an aqueous solution of NaCl (0.507 M) containing bacteria (O.D.₄₅₀: 0.5) was used in biofouling experiments. The high salinity waters were circulated from the reservoir through the stack at a flow rate of 300 mL/min. The compositions and concentrations of the solutions used in the experiments are shown in Table 6.2.

Table 6.2 Composition and concentration of solutions used in biofouling experiments.

	Feed solution	
	Low salinity water	High salinity water
Control experiment	NaCl (0.017 M)	NaCl (0.507 M)
Biofouling experiment	NaCl (0.017 M)	0.507 M NaCl which contains <i>P.putida</i> bacteria (<i>P.putida</i> O.D. ₄₅₀ :0.5)

Figure 6.4. shows the timeline for the preparation of bacterial suspensions and the biofouling experiments. *P. putida* was first inoculated into a modified FAB medium containing agar at a concentration of 15 kg/m³ for 6 h at 30 °C. Then, *P. putida* was precultured in the modified FAB medium for 18 h at 30 °C. The precultured bacterial suspension was diluted 50 times with the modified FAB medium. It was then cultured at 30 °C for 4 hours. Finally, the cultured bacterial suspension was diluted with modified FAB to an optical density (O.D.₄₅₀) of 0.5 and used for the experiments. The optical density was measured with a UV-Vis spectrophotometer (V-650, JASCO Corporation, Tokyo, Japan). The RED experiment was continued for 20 h.

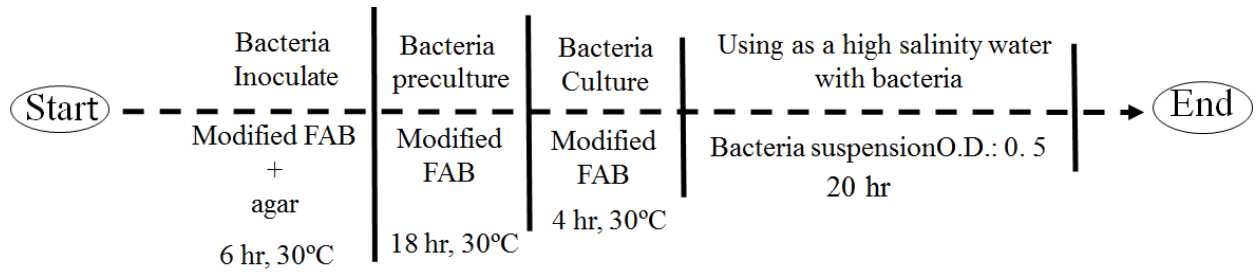


Fig. 6.4. Timeline of the preparation of bacteria suspension and the biofouling experiment under RED operation.

6.2.5. Evaluation of anti-biofouling during RED operation

RED was performed under constant load conditions with a fixed external resistance of 10 Ω . High and low salinity waters were circulated from the reservoirs through the high and low salinity compartments, respectively. Thus, the composition of the feed solution changed slightly during the experiment. The concentration of the high salinity compartment decreased, while the concentration increased in the low salinity compartment. The voltage across the membrane, V , was measured by high impedance potentiometer (Yokogawa- Hewlett- Packard, Tokyo, Japan) and recorded with a data logger during the biofouling experiment. In addition, the generated current (mA) was measured with a DC Amperemeter during RED.

Furthermore, the biofouling experiment was carried out under open circuit RED to evaluate the effect of electric field on biofouling. In open RED, there is no electric current flowing through the system, although there is a voltage difference across the stack.

The number of bacteria attached to the surface of the unmodified and PDA-modified membranes after RED was measured using a field emission scanning electron microscope (FE-SEM) (JSF-7500F; JEOL Co. Ltd., Tokyo, Japan) with an accelerating voltage of 7 kV. After the experiment, the membranes were rinsed with 0.85 wt% NaCl solution and immersed in 2.5% (v/v) glutaraldehyde solution for at least 10 min to fix the adhered bacteria, then dried overnight in a freeze dryer (FDU-1200 EYELA; Tokyo Rikakikai Co. Ltd, Tokyo, Japan) and coated with osmium tetroxide (OsO₄) prior to FE-SEM measurements. A thin OsO₄ layer (ca. 5 nm) was formed using an osmium coater (Neoc-STB; MEIWAFOSS Co. Ltd., Tokyo, Japan). The surface observed by FE-SEM was analyzed using Image J software to calculate the percentage of the surface covered with bacteria. The anti-biofouling properties of the AEM were evaluated from this coverage percentage.

6.3. Results and discussion

6.3.1. Biofouling behavior under immersion condition

First, the unmodified and PDA-modified membranes were immersed in a *P. putida* bacterial suspension (O.D.₄₅₀: 0.5) containing 0.507 M NaCl in order to confirm the effect of RED on biofouling. The bacterial suspension in this experiment was the same as the high salinity water containing bacteria that was used in the RED experiment (Table 6.2). Figure 6.5 shows the unmodified and PDA-modified AMX membrane surfaces as observed by FE-SEM after immersion for 20 h. The surface coverage percentages were 45.5% and 13.7% for the unmodified and PDA-modified membranes, respectively.

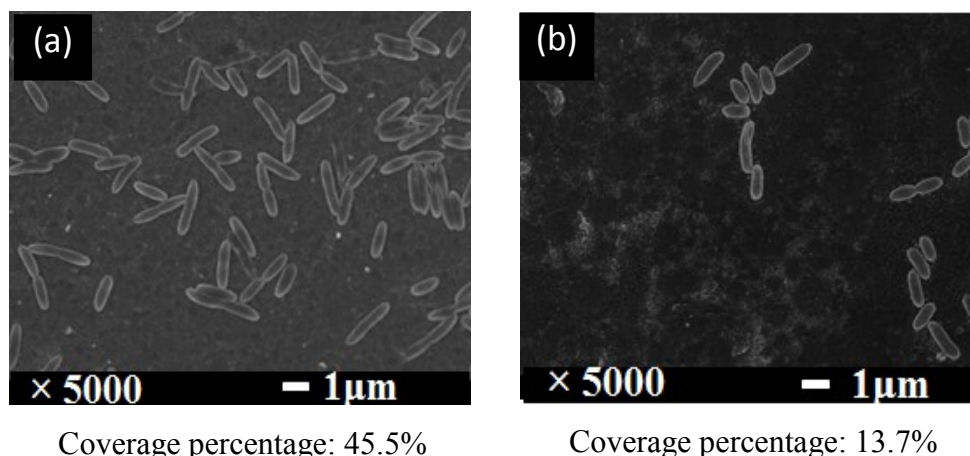


Fig. 6.5. FE-SEM images of (a) unmodified AMX membrane surface, (b) PDA modified AMX with PDA, after 20 h immersion into 0.507 M NaCl aqueous solution which contains *P. putida* bacterial suspension (O.D.₄₅₀: 0.5).

The results show that the attachment and growth of bacteria on the membrane surface was effectively suppressed by the PDA coating. The suppression of bacterial attachment was related to the improved hydrophilicity of the membrane and the presence of a negative surface charge layer on its surface [13,14]. Figure 6.6 shows the ζ potential and the hydrophilicity of modified AMX as a function of the dopamine concentration in the modification solution already reported in our previous paper [13]. A 0.1 kg/m³ dopamine solution was used for the surface modification in this work. As shown in Fig. 6. 6, even modification with low concentrations of dopamine led to the membrane surface becoming more hydrophilic and more negatively charged, which leads to the suppression of bacteria attachment.

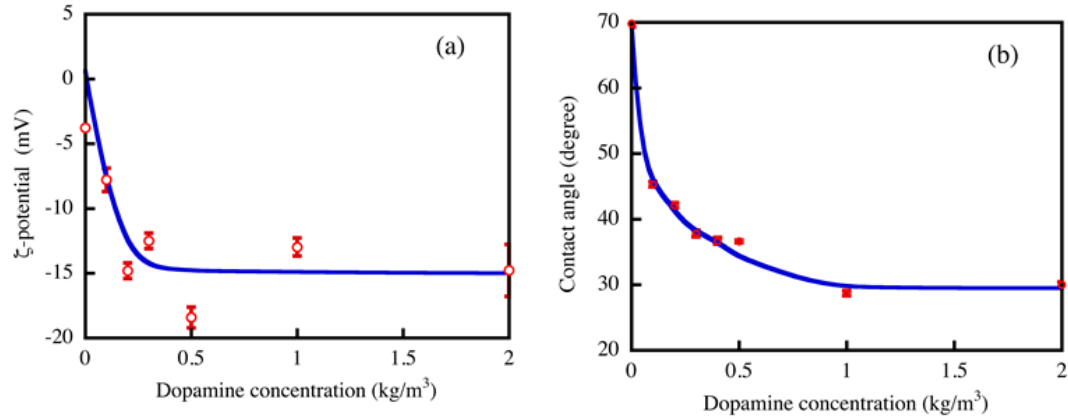


Fig. 6.6. (a) ζ -potential and (b) contact angle of modified AMX as a function of dopamine concentration [13].

6.3.2. Biofouling behavior under RED operation

To evaluate the anti-biofouling potential of the AEMs during RED, biofouling behavior was investigated using a RED stack similar to that shown in Fig. 6.3. The RED stack consists of a cell containing a CEM, an AEM, a high salinity compartment, and a low salinity compartment. The biofouling behavior of unmodified and PDA-modified AMX was investigated using two different high salinity waters, as shown in Table 6.2. In the control experiment, 0.507 M NaCl solution was used as the high salinity water, while in the biofouling experiment, a bacterial suspension of *P. putida* (O.D.₄₅₀: 0.5) containing 0.507 M NaCl was used instead. In each experiment, the high and low salinity waters were circulated from the reservoirs through each compartment for 20 h. The voltage (V) and current (mA) were measured under constant load conditions with a fixed external resistance of 10 Ω .

Figure 6.7 shows the change in voltage (V) (Fig. 6.7a) and electric current (mA)

(Fig.6.7b) over time for unmodified and PDA-modified AMX membranes during RED with different feed solutions. The initial voltage and current of the unmodified membrane were higher than those of the PDA-modified membrane, which is attributed to the thin PDA coating layer. The PDA layer gave a negative charge to the AEM, while unmodified AEM had a positive charge. The existence of the PDA layer also increased the membrane resistance. It has already been reported that the membrane resistance of unmodified AMX increased from 2.5 to 5.0 $\Omega \text{ cm}^2$ when modified with 0.1 kg/m³ of dopamine solution [13]. The voltage and current remained almost constant for both the unmodified and PDA-modified membranes over the 20 h of the control experiment. Thus, it is clear that the change in the feed concentrations due to circulation scarcely affects the RED performance. However, it was found that the voltage and current (Fig. 6.7A and B) of the RED decreased during the biofouling experiment. The reductions in voltage and current were significantly lower for the PDA-modified membrane than for the unmodified membrane, with the reduction in voltage and current being 0.008 V and 0.08 mA for the PDA-modified membrane, respectively, and 0.012 V and 0.63 mA for the unmodified membrane, respectively. This implies that the PDA-modified membrane possesses enhanced anti-biofouling properties when compared with the unmodified membrane, even during the RED process. The useful life of the PDA-modified membrane would therefore be longer than that of the unmodified membrane during RED because of the improvement in the anti-fouling properties by PDA coating.

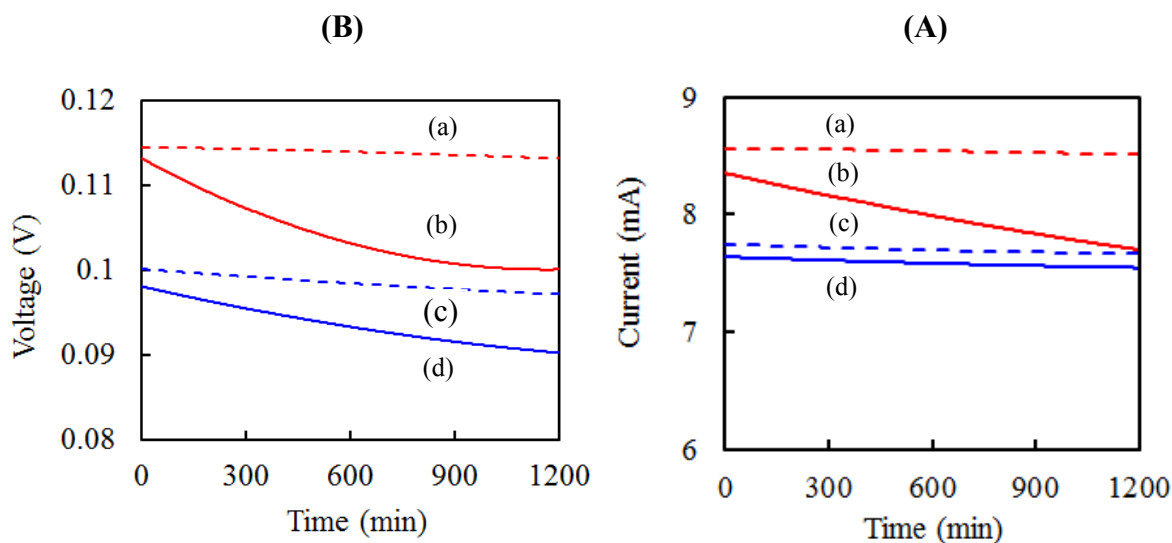


Figure 6.7 Changes in (A) voltage and (B) current during 20 h of RED for unmodified and PDA-modified AMX membranes for control tests and biofouling experiments. (a): Unmodified AMX (control), (b): Unmodified AMX (biofouling experiment), (c): PDA-modified AMX (control), (d): modified AMX (biofouling experiment).

Figure 6.8 shows FE-SEM images of unmodified and PDA-modified AMX membranes after 20 h of biofouling during RED. It is clear that the number of bacteria attached to the membrane surface was markedly decreased when the membrane was modified with 0.1 kg/m³ dopamine solution. The surface coverage percentages were 16.3% and 6.8% for the unmodified and PDA-modified membranes, respectively. Thus, the surface covered by bacteria was sufficiently decreased by the PDA coating.

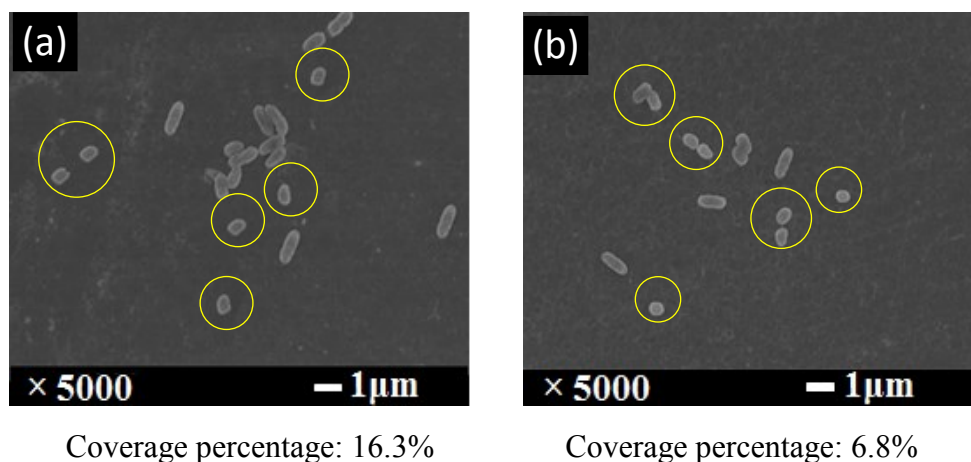


Figure 6.8 FE-SEM images of (a) an unmodified AMX membrane surface, and (b) a PDA-modified AMX membrane surface, after 20 h of biofouling with a *P. putida* bacterial suspension (O.D.₄₅₀: 0.5) during RED.

Furthermore, it can be seen from the comparison of Fig.6.8 with Fig.6.5 that the shape of some bacteria changed during RED (marked bacteria in Fig.6.8). The bacterial shape was rod-like after the immersion test, which is the normal shape of *P. putida*. However, the shape changed to spherical after RED operation. It is reasonable to consider that the bacteria shape was changed because an electric current flowed through the stack under RED operation. This phenomenon is consistent with previous reports. Liu et al. showed that current influenced the number and growth of bacteria (*Staphylococcus aureus*, *Staphylococcus epidermidis*, *Escherichia coli*, *Klebsiella pneumoniae*, and *Proteus mirabilis*) when applied for a long period (e.g., 24 h) [24]. Moreover, Luo et al. reported that electric current caused significant changes in the surface properties of bacteria and the shape of bacterial cells [25]. I also reported in my previous study that the application of direct electric current reduced biofouling during

the ED process and changed the bacteria shape [14]. During ED, the feed solution was a 0.05 M aqueous solution of NaCl containing *P. putida*. (O.D.₄₅₀: 0.5). The bacteria concentration was the same as that used in RED. The coverage percentages after 20 h of ED were 11.3% and 3.4% for the unmodified and PDA-modified membranes, respectively. The surface coverage in ED was lower than in RED. In addition, the change of bacterial shape was more pronounced in ED than in RED. These differences can probably be attributed to the different current densities and electric fields used for the RED and ED processes. The current density in ED process was 2 mA/cm², which was 5 times higher than the 0.4 mA/cm² used in the RED process. However, it is not clear whether electric current or electric field dominated the suppression of bacterial attachment and damaged the bacteria. Therefore, further investigation will be required to clarify this phenomenon.

6.3.3. Biofouling behavior under open circuit RED

In order to clarify the dominant parameter influencing bacterial attachment and shape, the anti-biofouling experiment was carried out under open circuit RED operation. This means that no electric current flows through RED stack, rather that only an electric field is generated. Thus, it is possible to evaluate the effect of the electric field on biofouling phenomena. Experimental conditions were the same as the system described in the previous section, but the circuit was open. Figure 6.9 shows the voltage generated (V) over time during open circuit RED with unmodified and PDA-modified AMX membranes. The initial voltages under open circuit conditions were higher than those seen for the RED process; because there was no external load, the maximum voltages could be obtained in the open circuit RED. In addition, the initial voltage generated for

the PDA-modified membrane was lower than that of the unmodified membrane due to the negative charge layer on the surface. It was found that the voltages generated for unmodified and PDA-modified membranes were almost constant during the experiment (i.e., over 20 h) for both the control and the biofouling experiments. This was because there was no electric current and thus the voltage did not change even if the membrane resistance was increased by biofouling.

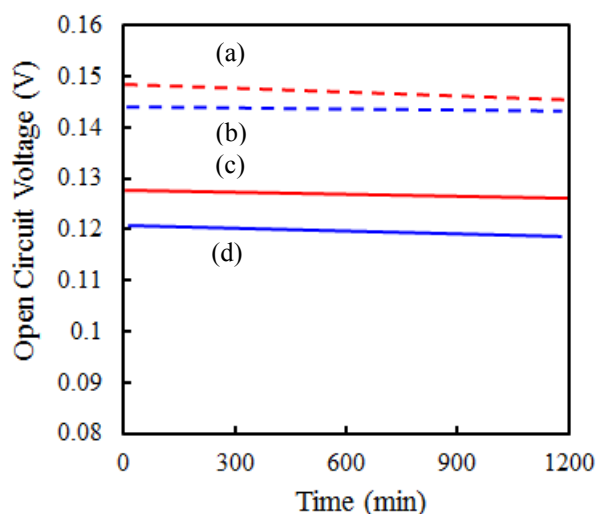


Figure 6.9 Change in voltage over time during open circuit RED for unmodified and PDA-modified AMX membranes using NaCl solution as a control and a bacterial suspension of *P. Putida* with O.D.₄₅₀ of 0.5 as a biofouling experiment. (a) Unmodified AMX (control), (b) Unmodified AMX (biofouling experiment), (c) PDA-modified AMX (control), (d) PDA-modified AMX (biofouling experiment).

Figure 6.10 shows FE-SEM images of unmodified and PDA-modified AMX membranes after biofouling experiments under open circuit RED conditions for 20 h. It is clear that the number of bacteria attached to the membrane surface was decreased by

PDA modification with 0.1 kg/m^3 of dopamine solution. The surface coverage percentages were 21.1% and 7.2% for the unmodified and PDA-modified membrane, respectively. These respective coverage percentages are higher than those seen for the RED operation shown in Fig. 6.8.

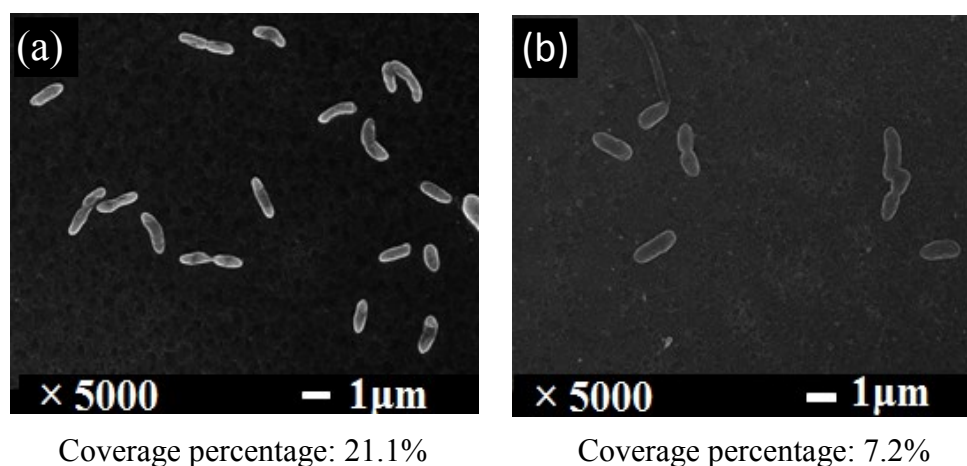


Figure 10 FE-SEM images of (a) an unmodified AMX membrane surface, and (b) AMX modified with 0.1 kg/m^3 PDA, after 20 h biofouling experiments with bacterial suspensions of *P. putida* (O.D.₄₅₀: 0.5) during RED in open circuit conditions.

Interestingly, Fig. 6.10 shows that bacterial shape was not changed under open circuit RED conditions. This indicates that the electric field in the open circuit RED does not affect the bacterial shape, but rather that the electric current changes the shape of bacteria.

6.3.4. Comparison of bacteria coverage percentages and bacteria shape changes in various conditions

Table 6.3 shows a summary of the biofouling experiments under different conditions (immersion, RED, and open circuit RED). The result of biofouling under ED operation [14] is also included in this table to allow comparison of this result with the new findings. In Table 6.3, it is found that the shapes of almost all attached bacteria were changed under ED conditions, while only some of them changed during RED. This can be attributed to the difference in the electric current densities, which were 2 mA/cm² during ED, but only 0.4 mA/cm² during RED. In the cases of open circuit RED and immersion, bacterial shape did not change, as there was no electric current under these conditions.

In addition, Table 6.3 shows that the bacterial surface coverage of PDA-modified membranes were lower than those of unmodified membranes under the same experimental conditions. This means that the modification of AMX with PDA improved its anti-biofouling properties under all conditions. The high hydrophilicity and negative charge of the PDA coating layer contributed to the improvement of the anti-biofouling properties [13, 26, 27].

The bacterial coverage percentages increased in the order of ED, RED, open circuit RED, and immersion conditions for both unmodified and PDA-modified AMX membranes. In the case of ED and RED, the electric current changed the bacterial shape, leading to a decrease in bacterial attachment. Thus, the higher electric current used in ED was more effective at reducing the bacterial coverage, and the bacterial attachment amount was lowest in ED. The bacterial coverage in open circuit RED was lower than

that under immersion conditions. This indicated that the electric field reduced bacterial attachment, although the bacterial shape was not changed by the electric field, as mentioned above. The reason for this phenomenon is not clear at this time. One possible reason is that the electric field polarizes the bacterial cells and changes their characteristics. The bacterial activity is then decreased and consequently the bacterial attachment is reduced by electric field. Overall, biofouling in the RED process was significantly decreased by PDA coating, electric current, and electric field effects.

Table 6.3. Bacteria coverage percentages and bacteria shape changes for unmodified and PDA- modified membranes in different experimental conditions after 20 h operation.

membrane	Operation	Feed solution	O.D. ₄₅₀	Coverage %	Initial electric field density (V/cm)	Initial Current density (mA/cm ²)	Shape Change
Unmodified AMX membrane	ED [13]	Bacteria + NaCl (0.05 M)	0.5	11.3	0.351	2.00	++
	RED	Bacteria + NaCl (0.507 M)	0.5	16.3	0.137	0.41	+
		open circuit	0.5	21.1	0.156	0.00	-
		RED	0.5	21.1	0.156	0.00	-
	Immersion	Bacteria + NaCl (0.507 M)	0.5	45.5	0.000	0.00	-
0.1 kg/m ³ PDA modified AMX membrane	ED [13]	Bacteria + NaCl (0.05 M)	0.5	3.4	0.437	2.00	++
	RED	Bacteria + NaCl (0.507 M)	0.5	6.8	0.120	0.38	+
		open circuit	0.5	7.2	0.147	0.00	-
		RED	0.5	7.2	0.147	0.00	-
	Immersion	Bacteria + NaCl (0.507 M)	0.5	13.7	0.147	0.00	-

++: almost all, +: some, -: not happen

6.4. Conclusion

In this study, I examined biofouling during RED and attempted to improve the anti-biofouling properties of AEM by PDA coating. For comparison, open circuit RED (i.e., without an electric current) and immersion tests were carried out.

It was found that PDA modification improved the anti-biofouling properties of AMX membranes during RED, open circuit RED, and immersion. For modified membranes, the ability to reduce bacterial attachment decreased going from RED to open circuit RED to immersion conditions. The most pronounced reduction in bacterial attachment was observed for RED with both an electric current and electric field. In this operation, the bacterial shape changed due to the generated electric current. The electric field generated in open circuit RED was also beneficial for reducing bacterial attachment. The largest amount of bacteria was attached on the membrane surface under immersion conditions, where there was neither an electric current nor an electric field.

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Chapter 7

Conclusion

Water is one of the most precious and essential sources for beings including human life. However, global water shortage has become a critical problem. Electrodialysis (ED) is one of the useful membrane processes to produce a drinking water from seawater, brackish water and other water sources using anion and cation exchange membranes. ED possess notable and unique advantages such as high water recovery, removing harmful monovalent anions such as F^- and NO_3^- , wiping heavy metals and preparation of softening water than that other membrane processes. However, it is still required to enhance some properties such as the monovalent anion permselectivity and anti-fouling properties of anion exchange membrane (AEM) in order to improve ED performance.

One of the most important properties of AEM that should be improved is monovalent anion selectivity. A high monovalent anions selectivity (relative to multivalent anions) assists to improve two properties. First is removing harmful ions with high current efficiency. The harmful anions such as NO_3^- and F^- should be removed to make a safe potable water. Second is the preventing an inorganic fouling by reducing

scale formation. In general, AEMs are a multivalent anion selective. Meanwhile, multivalent anions like SO_4^{2-} are also removed from a feed solution. If the amount of SO_4^{2-} ions is increased too much in the concentrate compartment, a precipitation of calcium sulfate (CaSO_4), that is called a scaling, takes place in the concentrate compartment and ED performance decreases. Therefore, it is required to improve the monovalent anion selectivity to increase the ED performance

➤ **In chapter 2**, I theoretically investigated the effect of parameters, which influence on the anion permselectivity using circuit model. It was found that the electric resistance of system and permselectivity are affected by dilute compartment resistance. In addition, I showed that the charge density of AEM in the system that contained a mixed solution of monovalent and multivalent anions controls the permselectivity. The monovalent permselectivity of AEM could be improved by AEM surface modification through a negativity charged layer. This layer acted as an additive electric resistance for the AEM. The amount of multivalent anions partitioned into the negatively charged layer was lower than that of monovalent anions because of Donnan exclusion. Consequently, this phenomenon increased the membrane resistance for multivalent anions and decreased the flux of multivalent anions through the AEM. Therefore, monovalent anion selectivity improved. Furthermore, I showed that it is possible to roughly predict the anion permselectivity by measuring the membrane resistance of each electrolyte with a single electrolyte solution.

➤ **In chapter 3**, in order to experimentally verify the theoretical discussion and predictions, I modified a commercial anion exchange membrane (AMX) with polydopamine (PDA). PDA induced a negatively charged layer on AMX surface. I

measured the permselectivity of the PDA-modified AEM for NO_3^- , F^- , and SO_4^{2-} relative to Cl^- .

In this chapter, I could experimentally confirm the following theoretical predictions:

- I. The selectivity of monovalent anions will be improved by modifying the AEM surface with a negatively charged layer
- II. This surface modification will not affect the selectivity between monovalent anions.
- III. It will be possible to roughly estimate the permselectivity of anions by measuring the membrane resistance for each electrolyte with a single-electrolyte solution.

In addition, I analyzed the experimental data with our theoretical model and determined the charge density of PDA layer of the AMX membrane surface. The theoretical curves calculated with the obtained charge density of the negatively charged layer fit the experimental results well. I showed that the monovalent anions selectivity is determined mainly by the electric resistance of the negatively charged layer and the dilute compartment. Altogether, the surface modification of the AEM with a negatively charged layer is a very beneficial method to improve the monovalent anions selectivity in the ED process.

Another serious problem of anion exchange membranes (AEMs) to improve ED performance is membrane fouling. Membrane fouling, which leads to increase membrane resistance and running costs, is a complex issue that can be divided to inorganic fouling, organic fouling and biofouling.

I presented in chapter 3 that the monovalent anions selectivity of AEMs were improved by the surface modification. Improvement of monovalent anions permselectivity result to decrease inorganic fouling by reducing scale formation. When harmful anions such as NO_3^- and F^- remove from the feed solution to produce safe drinking water, multivalent anions like SO_4^{2-} can not remove from the feed solution. Because PDA-modified AEMs are a monovalent anions selective membrane. Thus, SO_4^{2-} ions concentration is reduced in the concentrate compartment and prevent the precipitation of inorganic materials (scaling) such as calcium sulfate (CaSO_4) in the concentrate compartment.

➤ In chapter 4, I could sufficiently improve the anti-organic fouling property of commercial anion exchange membrane (AMX) via PDA surface modification. PDA coating gives hydrophilic negatively charged layer to the membrane surface which led to reduce organic fouling resistance. The anti-organic fouling property of AMX was evaluated with transition time (i.e. the time elapsed before fouling take place, t_{tran}). The maximum transition time (i.e. t_{tran} : 300 min) anti-organic fouling was determined for AMX membrane modified with 0.1 kg/m^3 dopamine aqueous solution. This concentration was considered as an optimal dopamine concentration. In addition, the organic fouling mechanism was evaluated using model that previously proposed. Furthermore, it was experimentally confirmed that the modified membrane was highly stable.

➤ In chapter 5, same as chapter 4, commercial anion exchange membrane (AMX) was modified with PDA in order to increase anti-adhesion properties that leads to improve anti-biofouling potential of the membrane. The biofouling property was

evaluated using a static adhesion test. The bacteria attached on the membrane surface was observed by confocal laser scanning microscopy (CLSM). Then, the total cell volume and coverage percentage were calculated using COMSTAT software. The results showed that the number of bacteria attached on the membrane surface significantly decreased by PDA modification and found that 0.1 kg/m^3 is an optimal concentration of dopamine.

Moreover, biofouling during ED operation was evaluated by the increase of transmembrane potential due to the increase of electric resistance of the membrane caused by biofouling. The voltage did not change during ED operation even for unmodified membrane. It indicates that direct electric current (DC) also decreases biofouling. Thus, biofouling may scarcely occur in a real ED operation. For further investigation, fouled membranes were then observed by scanning electron microscope (SEM). The coverage percentage was determined by analyzing the SEM images. Although the bacteria concentration under ED operation was 10 times higher than that static adhesion test, the coverage percentage was smaller than that of static adhesion test. Moreover, the results revealed that the coverage was minimum for a surface modified with 0.1 kg/m^3 of dopamine concentration which is the same as the static adhesion test and the organic fouling. In addition, in comparison with static adhesion test (immersion), bacteria shape completely changed due to DC effect. Therefore, PDA layer and DC suppressed bacteria attachment on AEM surface and sufficiently improves anti-biofouling of AMX membrane during ED performance.

Considering all of the results, including those reported in chapters 3 and 4, it is concluded that 0.1 kg/m^3 is the optimal concentration of dopamine for membrane

modification to improve overall ED performance. Because the surface modification with 0.1 kg/m^3 dopamine solution simultaneously improved anti-biofouling, anti-organic fouling, and monovalent anion permselectivity. Improvement in monovalent anion selectivity is expected to decrease scale formation and consequently improves anti-inorganic fouling properties.

The other global serious problem is earth warming and air pollution due to using fossil fuels and increasing of energy demanding due to reduction of these sources which caused to generate the blue energy. Mixing two water streams with different salt concentrations (e.g., sea and river water) have potential to generate salinity gradient energy (SGE). One of the main techniques for extracting energy from a salinity gradient energy is reverse electrodialysis (RED). A RED is an electrochemical process to convert a salinity gradient energy to an electric energy. However, in the RED system, a biofouling of anion exchange membrane (AEM) is very severe problem that declines the RED performance.

➤ In chapter 6, I studied the biofouling phenomena of AEM under RED operation and improved anti-biofouling property of AEM with surface modification. As same as previous chapters, a commercial anion exchange membrane (AMX) was modified with optimal concentration of dopamine solution (0.1 kg/m^3). The biofouling behavior of RED process, open circuit RED (without electric current) and immersion were evaluated by the bacteria surface coverage percentages obtained from the surface analysis of SEM images of fouled AEM surface.

All results showed that the number of bacteria attached on the membrane surface significantly decreased by PDA modification. For modified membrane, bacteria amount

attachment order was RED < open circuit RED < immersion condition. In the case of RED operation, reduction of the bacteria attachment was obviously due to present of electric current and electric field. In RED operation, the bacteria shape was changed due to the applied of electric current. The electric field applied in open circuit RED was also useful to reduce the bacteria attachment. The maximum amount of bacteria attached on the membrane surface belongs to the immersion condition that no electric current and electric field. Thus, biofouling is significantly decreased in the RED process by PDA coating, electric current and electric field effects.

A comparison of bacteria coverage percentages and bacteria shape of unmodified and PDA- modified AMX membrane for various operations (ED, RED, open circuit RED and immersion) are summarized as blow:

- I. In all operations, the bacteria surface coverage of PDA-modified membrane is lower than that of unmodified membrane under the same experimental condition.
- II. The order of bacteria coverage is ED < RED < open circuit RED < immersion condition for both unmodified and PDA- modified AMX membrane.
- III. The shape of attached bacteria was almost changed under ED operation, while some of them changed under RED operation.
- IV. The shape of attached bacteria did not change under open circuit RED operation and immersion condition.
- V. The electric current is dominant parameter for changing the bacteria shape.
- VI. The biofouling is significantly suppressed in all processes (ED, RED, open circuit RED and immersion) by PDA coating, electric current and electric field effects.

List of Publications

Chapter 2 Theoretical study of the permselectivity of an anion exchange membrane in electrodialysis.

Ryosuke Takagi, Mahboobeh Vasselbehagh, Hideto Matsuyama, Journal of Membrane Science 470 (2014) 486–493.

Chapter 3 Surface modification of an anion exchange membrane to improve the selectivity for monovalent anions in electrodialysis – experimental verification of theoretical predictions.

Mahboobeh Vasselbehagh, Hamed Karkhanechi, Ryosuke Takagi n, Hideto Matsuyama, Journal of Membrane Science, 490 (2015) 301–310.

Chapter 4 Improved antifouling of anion-exchange membrane by polydopamine coating in electrodialysis process.

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