

Thesis for the Master's degree

Development and performance evaluation of  
hydrocarbon-based proton exchange membranes for  
electrobiofuels production in microbial electrolysis cells



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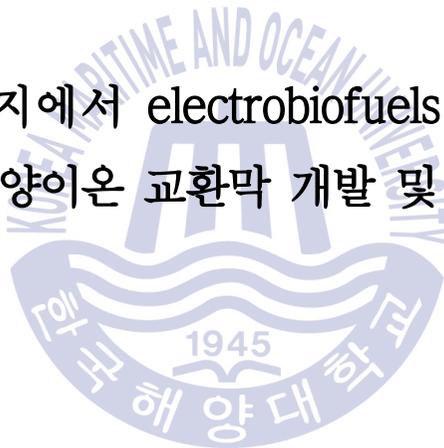
Graduate School of Korea Maritime and Ocean University

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미생물전해전지에서 electrobiofuels 생산을 위한  
탄화수소계 양이온 교환막 개발 및 성능 평가



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## Abbreviations

AD, anaerobic digestion;

AFM, atomic force microscopy;

ARB, anode respiring bacteria;

DMAc, N,N-dimethylacetamide;

DS, degree of sulfonation;

EDX, energy-dispersive X-ray;

FE-SEM, field emission scanning electron microscope;

HER, hydrogen evolution reaction;

IEC, ion exchange capacity;

MEC, microbial electrolysis cell;

MFC, microbial fuel cell;

NHE, normal hydrogen electrode;

PEM, proton exchange membrane;

PIN, polyimide nanofiber;

PTFE, poly(tetrafluoroethylene);

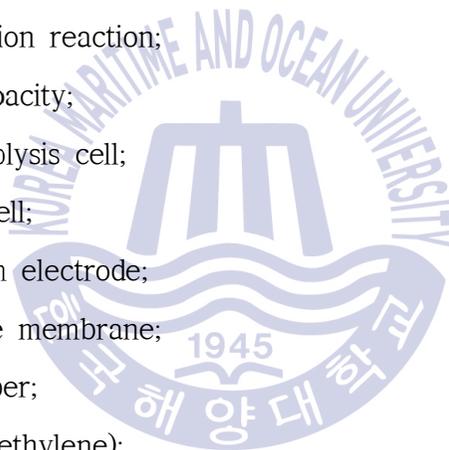
PVDF, polyvinylidene fluoride;

s-MPO, sulfonated mesoporous organosilicate;

SPAES, sulfonated poly(arylene ether sulfone);

SPEEK, sulfonated poly(ether ketone);

WU, water uptake;



# Development and performance evaluation of hydrocarbon-based proton exchange membranes for electrobiofuels production in microbial electrolysis cells

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## Abstract

A sulfonated poly(arylene ether sulfone) (SPAES)/polyimide nanofiber (PIN) composite proton exchange membrane was developed for use in microbial electrolysis cells (MECs), where diverse cations that compete with proton coexist in high concentrations. It was fabricated by impregnating SPAES as a proton-conducting polymer into PIN as a supporter for mechanical reinforcement. The membrane showed excellent mechanical and dimensional stability (tensile strength > 40 MPa) due to membrane reinforcement by nanofibers, despite having a high water uptake ( $35 \pm 3\%$ ) and ion exchange capacity ( $2.3 \pm 0.3$  meq/g). This novel membrane was highly selective for protons while excluding other competing cations; thus, it significantly mitigated the proton accumulation problem in the anode when applied to actual MECs. In addition to 1.5-fold greater proton transport, the SPAES/PIN membrane exhibited 3-

10-fold less undesirable crossover of other cations depending on the species and 2-2.5-fold less gas permeability compared to Nafion-211 membrane. The application of this membrane improved hydrogen production efficiency of MEC by 32.4% compared to Nafion-211 and better hydrogen purity (90.3% for SPAES/PIN vs. 61.8% for Nafion-211). Therefore, this novel membrane has good potential for MEC applications, especially when protons and other competing cations are present together, due to its superior proton selectivity.

**Key words:** Microbial electrolysis cells; Hydrocarbon-based proton exchange membrane; Ion cluster channel; Hydrogen gas; Sulfonated poly(arylene ether sulfone)



# 미생물전해전지에서 electrobiofuels 생산을 위한 탄화수소계 양이온 교환막 개발 및 성능 평가

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초록

Sulfonated poly(arylene ether sulfone) (SPAES)/polyimide nanofiber (PIN) 양이온 교환 복합막은 다양한 양이온들이 공존하는 미생물전해전지 (Microbial electrolysis cells; MECs)에서 수소 이온을 효과적으로 전달하기 위해 개발되었다. 이 탄화수소계 양이온 교환 복합막은 물리적 강도를 보강하기 위한 지지체로 PIN을 사용하였고, PIN을 양이온 전도성 중합체인 SPAES에 함침 시켜 제조하였다. 이렇게 개발된 복합막은 높은 수분 흡수 능력( $35 \pm 3\%$ ) 및 이온 교환 능력( $2.3 \pm 0.3 \text{ meq/g}$ )을 가짐에도 불구하고, PIN에 의해 우수한 치수 안정성(인장 강도 > 40 MPa)을 나타냈다. 또한, 다른 경쟁 양이온들의 전달은 배제하면서 수소 이온을 선택적으로 전달하였는데 기존에 미생물전해전지에서 대표적으로 사용하던 불소계 양이온 교환막인 Nafion-211에 비해 수소 이온을 1.5배 빠르게 전달하였으며, 바람직하지 않은 다른 경쟁 양이온들의 전달과 기체 투과도는 각각 3-10배, 2-2.5배 더 적은 것으로 나타났다.

따라서, 미생물전해전지에 개발된 복합막을 적용하였을 때 anode에서 수소 이온이 축적되는 문제를 상당히 완화시켰고, Nafion-211을 적용했을 때

보다 Cathode에서 수소 가스 생산 효율이 32.4% 향상되었으며, 발생한 수소 가스의 순도도 대폭 증가하였다(Nafion-211의 경우 61.8% vs SPAES / PIN의 경우 90.3%). 결론적으로 이 새로운 탄화수소계 양이온 교환 복합막은 우수한 수소 이온의 선택적 전도성과 높은 치수 안정성 그리고 낮은 기체 투과도로 인해 미생물전해전지 분야에서 높은 이용 가능성을 지니고 있는 것으로 판단된다.

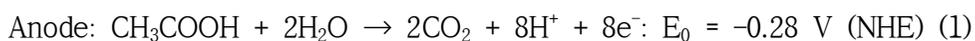
**주제어:** 미생물전해전지, 탄화수소계 양이온 교환막, 이온 전달 채널, 수소 가스, Sulfonated poly(arylene ether sulfone) (SPAES)



## Chapter 1. Introduction

Microbial electrolysis cells (MECs) represent an attractive green energy technology that can convert organic waste to a wide range of value-added products via specific microbes (i.e., exoelectrogens or biocatalysts) and a small input of electric energy [1, 2]. Hydrogen gas is the most common product of MECs, but MECs using biocatalysts can also produce other valuable chemicals, such as methane, ethanol, butanol, hydrogen peroxide, and acetate, using diverse types of final electron acceptors.

The basic components of a MEC are two electrodes (i.e., anode and cathode), a membrane, exoelectrogens, and a power supply. In a MEC, exoelectrogens, electrochemically active bacteria growing on the anode, convert the substrate into protons ( $H^+$ ), electrons ( $e^-$ ), and  $CO_2$ , and then those produced protons and electrons are transferred to the cathode and recombine to produce hydrogen or other value-added chemicals under the assistance of the power supply [3-6]. Typical half reactions in the electrode are shown in the following equations (1) and (2) using acetate as an example substrate:



A proton exchange membrane (PEM) is one of the key components of MECs; this plays the role of a separator between the anode and cathode to avoid short circuits while transporting protons produced in the anode

to the cathode compartment to generate hydrogen gas. Especially in the case of value-added chemical-producing MECs, it is commonly used to improve the purity of products (e.g., hydrogen) in the cathode by preventing an undesirable interchange of gases produced in both the anode and cathode. In the anode compartment of the MEC, various gases ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , etc.) are generated, since not only exoelectrogens but also other microbes (typically methanogens) grow together; if they are intermixed with the hydrogen gas produced at the cathode, an additional, expensive refining process is required for practical utilization. Therefore, although there are some concerns related to using a membrane in MECs, such as the potential losses attributed to the inclusion of the membrane and pH gradient formation across the membrane because of the hindered proton transport [2, 5, 6], utilization of a PEM can provide many advantages in MEC operation, especially in cases where mixing of gases must be thoroughly prevented.

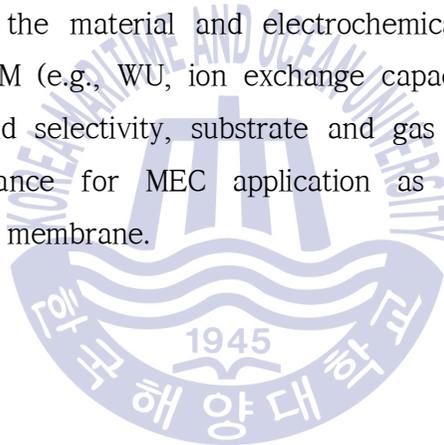
In MECs, the membranes used in conventional hydrogen fuel cells are also often used as a PEM. However, the PEM used in MECs requires completely different characteristics from that used in hydrogen fuel cells, because microorganisms are used as biocatalysts in the anode. In the anodic solution of the MEC, to grow anode microorganisms, various cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , etc.) exist at a significantly higher concentration (typically 105 times) than that of protons; those cations hinder the transport of protons by competing for the transporting channels (i.e., negatively charged sulfonate groups;  $\text{HSO}_3^-$ ) of the membrane [2, 6, 7]. As a result of losing the contact chance of protons being transported from the anode to the cathode chamber, protons are continuously accumulated in the anode chamber and results in a serious pH decrease, while a corresponding pH increase occurs in the cathode chamber [6].

Such a serious pH drop adversely affects the anode bacteria, thereby deteriorating the performance of the MECs. Therefore, proton selectivity—which selectively passes protons while excluding other competitive cations—is an important requirement for the PEM in the application to MECs. However, so far, studies on PEMs have mainly focused on proton conductivity improvement from the perspective of hydrogen fuel cells using pure protons; in contrast, little research has been conducted on the proton selectivity problem in MECs, where complex cations coexist with protons. Furthermore, easy gas diffusion across the membrane adversely reduces hydrogen purity by mixing with the gases (CO<sub>2</sub>, CH<sub>4</sub>, etc.) diffused from the anode. Therefore, the essential requirements of an ideal PEM for use in MECs are high proton selectivity, low gas and substrate crossover, and inexpensive and strong mechanical properties.

As a PEM, Nafion (DuPont) is the most widely used; this is a perfluorosulfonic acid membrane consisting of a hydrophobic fluorocarbon backbone (-CF<sub>2</sub>-CF<sub>2</sub>-) and hydrophilic side chains with sulfonic functional groups (-HSO<sub>3</sub>) [6–8]. Nafion exhibits a phase-separated morphology of discrete hydrophobic and hydrophilic regions. The hydrophobic region is the polymer fluorocarbon backbone, while the hydrophilic region, a cluster for ion transport, is composed of the ionic groups and their counter ions. Based on the latest research on PEMs for fuel cell application, aspects of Nafion's performance, such as the proton conductivity and mechanical properties, have been improved by adopting diverse approaches, including doping and blending [10], compositing [8, 11], and pretreatment [12]. To improve membrane performance, Wang et al. [11] modified the proton transfer channel in Nafion using 3,4-dimethyl-benzaldehyde; through this modification, the diameter of the channel could be enlarged due to the enhanced hydrophobic-hydrophilic

separated structure. However, the Nafion membrane has some limitations for use in MECs due to its low proton selectivity, the high crossover tendency of the gas and substrate, and its high production cost. To overcome these drawbacks, sulfonated hydrocarbon-based polymers, mainly sulfonated polyether ether ketone (SPEEK) and sulfonated poly(arylene ether sulfone) (SPAES), have been intensively investigated as alternative proton-conducting PEM materials to fluorocarbon-based Nafion [6, 13–18]. Compared with Nafion, SPAES exhibits a significant difference in the extent of hydrophobic–hydrophilic microphase separation due to its unique material properties, showing lower hydrophobicity of its aromatic hydrocarbon backbone. Thus, the clustering of hydrophilic domains, which plays a key role in proton conduction in PEMs via the Grotthuss mechanism [19], can be formed in more branched, narrower, and more tortuous configurations in the SPAES microstructure. These more branched, more tortuous hydrophilic clusters (channels) lead to the improvement of proton selectivity while lowering undesirable gas or substrate crossover. However, despite its advantages, SPAES has an inherent mechanical weakness due to an excessive water uptake (WU) and swelling feature, as the SPAES membrane needs to be designed to have more ion exchange capacity (IEC) to obtain comparable (or even higher) proton conductivity to Nafion. This higher IEC due to excessive sulfonation causes mechanical instability attributed to excessive WU, so the membrane can easily be delaminated or torn during its application. According to an intensive review on hydrocarbon-based polymer electrolyte membranes [9], membrane's morphology affects strongly electrochemical properties (e.g., ion conductivity, water transport, etc.) and membrane stabilities (e.g., water uptake, dimensional swelling behavior, mechanical strength, etc.).

To solve the physical weakness while taking advantage of SPAES' unique superior proton transfer characteristics, we developed a new SPAES/polyimide nanofiber (PIN) composite membrane (hereinafter referred to as a SPAES/PIN composite membrane) for MEC application. In the SPAES/PIN composite membrane, PINs, which are highly compatible with SPAES, are embedded as a membrane substratum in the center of the SPAES polymer layer to improve mechanical strength and dimensional stability. Thus, the proton is transferred through SPAES polymer, and the physical stability of the membrane is maintained by the PINs. The purpose of this paper is to report the results of an intensive study on the material and electrochemical properties of the developed novel PEM (e.g., WU, ion exchange capacity, tensile strength, proton transport and selectivity, substrate and gas crossover, etc.) and its actual performance for MEC application as compared with the conventional Nafion membrane.



## Chapter 2. Literature review

### 2.1 Microbial electrolysis cells (MECs)

The anaerobic digestion (AD), one of the biological anaerobic treatments, is now regarded as a desirable recovery technology for potential energy from the wastewater. During the past decade, there has been an emergence of a new high potential bio-based technology for wastewater treatment called bioelectrochemical systems (BESs) and resources recovery. BESs are able to be categorized into microbial fuel cells (MFCs) or microbial electrolysis cells (MECs) depending on their operation mode: galvanic (MFCs) or electrolytic mode (MECs) (Fig. 2.1) [20]

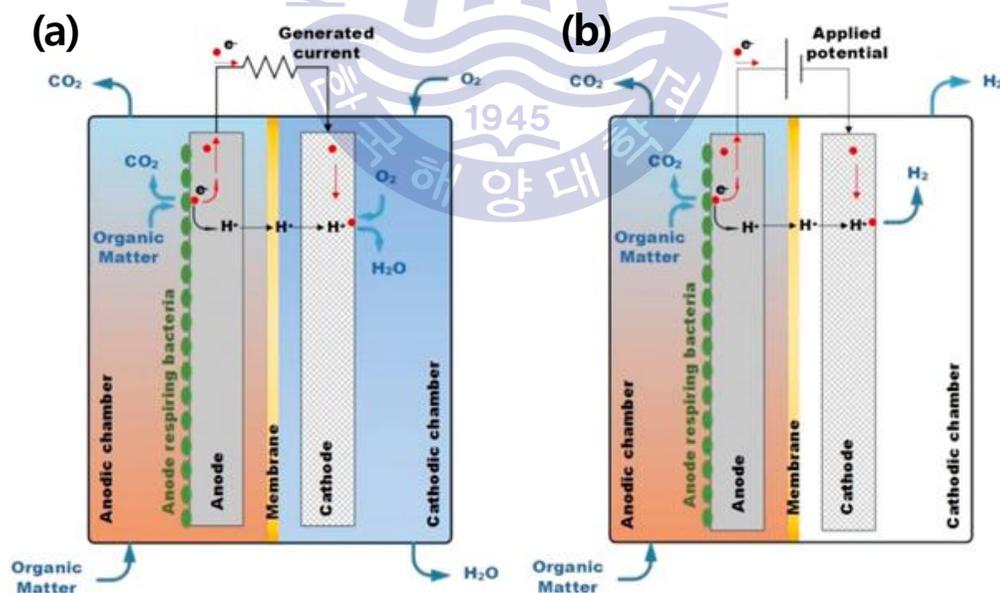


Fig. 2.1. Schematic representation of (a) electricity production and (b) hydrogen production through MFC and MEC respectively. [20]

The energy recovery from the wastewater using MECs has been preferred than MFCs in terms of economic, environmental, and technical value despite of on-going debates on their evaluation [21-24]. This preference depends largely on the product obtained from the system (hydrogen, methane, ethanol, hydrogen peroxide, etc). Particularly, hydrogen is a crucial resource in many strategic industrial sectors, and its high energy yield is a highly attractive characteristic which possibly lead to a replacement of the current energy sources in near future [25].

### 2.2.1 Basic principles

BESs, as electrochemical systems, involve the electrochemical interactions with microorganisms in at least one of the electrode reaction. In most of the cases, anode respiring bacteria (ARB) like *Geobacter* spp. which transfer the electrons from a biodegradable substrate to a solid electrode are essential in the anodic reaction. The mechanism of MFCs and MECs are schematically represented in Fig. 2.1. MFCs and MECs have quite similar reactions at biotic anodes.

Carbon dioxide, protons and electrons are the major by-products of ARB metabolism. Among them, electrons are transferred to the anode and then flow to the cathode through the external circuit. In MFCs, presence of oxygen in the cathode causes the electron flow due to the reduction reaction, thereby producing electricity. On the other hand, MECs without any oxygen in the cathode require an external power source of about 0.3-0.8V to activate the anodic electrode reaction. Therefore, production of value-added chemicals such as hydrogen, ethanol, and butanol becomes possible based on this mechanism [26-28].

**Table 2.1.** Summary of the products from MECs platform.

Products	MEC reactor	Electron acceptor	Cathode	Voltage applied (V)	Production rate (mmol/L)	Ref.
Methane (CH <sub>4</sub> )	Single/Two-chamber	CO <sub>2</sub>	Biocathode	0.7 – 1.0	0.06	[29]
Ethanol (C <sub>2</sub> H <sub>6</sub> O)	Two-chamber	Acetate	Biocathode	0 – 0.55	0.00003	[30]
Formic acid (CH <sub>2</sub> O <sub>2</sub> )	Two-chamber	CO <sub>2</sub>	Pb	1.13	0.09	[31]
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	Two-chamber	O <sub>2</sub>	Carbon cloth	0.5	1.17	[32]
Acetate (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> )	Two-chamber	CO <sub>2</sub>	Graphite sticks	0.4	n/a	[33]

### 2.2.2 Key influence factors

The selection of the suitable materials will decide the success of MEC designs that can meet the specific requirements of active components such as anodes, cathodes, and membranes.

#### 1) Anodes

The requirements for the anodic electrode materials in MECs are as follows: i) the high conductivity; and ii) the high biocompatibility of the surface that inhibits the growth and adhesion of the electrically active microorganism; iii) absence of clogging due to overgrowth of microorganisms and iv) chemical and biological stability and durability. Also, it should be easy v) to make the shape of electrode and vi) to expand the scale [34].

Carbon-based materials are the most suitable and widely used electrode materials under the criteria mentioned above. In parallel with this research, non-carbon-based materials including titanium and stainless steel as anodes have been examined. Although their conductivity is advanced to that of carbon-based materials their performance is mostly poor, probably because of their smaller surface area and surface properties that are much less suitable to biofilm development [35]. Carbon-based materials generally utilized in lab-scale tests are carbon felt [36, 37], graphite plates [24] and graphite fibers [38]. Moreover, Graphite granules [39] and granular activated carbon [40] have been appeared as appropriate candidates for anode materials because they characteristically have large surface area.

In addition to the study on the anode material, the surface modification methods such as acid treatment [41], heat treatment [42], ammonia treatment [43], surfactant treatment [44], electrochemical oxidation [45] and reduction [46] have been developed to increase the surface area of anodes, to stimulate adhesion of microorganisms and electrons transfer, or to enhance biocompatibility.

## 2) Cathodes

Carbon-based materials are mostly suitable not only for anodes but for cathodes when few modifications are made. The major requirement for a catalyst is to drive the hydrogen evolution reaction (HER) at low over-potentials. The identical reaction could be achieved by using noble metals such as platinum and palladium. However, they are not economically efficient as being expensive metals. [47]

In order to mitigate this problem, Some of the alternatives to Pt-based

cathodes such as Ni or MoS<sub>2</sub>-based materials, stainless steel alloys and other transition metals alloys are proved to be suitable due to their easiness of synthesis, low cost, stability and low over-potentials [48-50]; Moreover, specific microorganisms like hydrogen-producing microbes are used and cathode is used as an electron donor. Furthermore, it has been reported that this kind of biotic cathodes outperform traditional abiotic cathodes in terms of high-value energy production rate and efficiency [51,52].

**Table 2.2.** Performance comparison of different cathode catalysts

<b>Cathode material</b>	<b>MEC reactor</b>	<b>Cathode potential (mV vs SHE)</b>	<b>Applied potential (mV)</b>	<b>Coulombic efficiency (%)</b>	<b>Hydrogen recovery (%)</b>	<b>Ref.</b>
Carbon cloth with Pt	Single-chamber	n/a	800	96.8 ± 1.4	96 ± 1.1	[53]
Stainless steel	Single-chamber	n/a	900	87 ± 5	n/a	[54]
Stainless steel brush	Single-chamber	n/a	600	n/a	84	[43]
Ni foam	Two-chamber	n/a	1000	n/a	90	[55]
Biocathode	Two-chamber	-710	500	92 ± 6.3	57 ± 0.1	[56]
Biocathode	Two-chamber	-750	n/a	~80	n/a	[57]
Biocathode	Two-chamber	-590	n/a	54	n/a	[58]

### 3) Membranes

Initially, proton exchange membranes (PEMs) were used to isolate the anode and cathode electrolytes in hydrogen-producing MECs [2, 59, 60]. The major benefit of using PEMs is that they optimize the working condition such as low pH and high ionic concentration on the cathode area without affecting the microbial communities on the anode while obtain comparatively pure hydrogen.

On the other hand, MECs without membrane enhance the hydrogenotrophic methanogen group which utilize the hydrogen and produce methane, therefore downgrade the hydrogen gas purity.

#### 2.2 Hydrocarbon-based proton exchange membrane

The PEM should be mechanically and chemically stable in aqueous system while maintaining its main roles of proton exchange and reactant gases separation from each chamber [61]. Nafion is one of the most common type of the PEM, first developed by Dupont Inc. in late 1960, serving excellent proton conductivity and chemical and electrochemical stability. However, Nafion still has some downsides such as substrate crossover, low proton selectivity, as well as high cost.

For that reason, development of replacements to Nafion is inevitable. In recent years, sulfonated aromatic hydrocarbon polymer electrolytes such as poly(arylene ether)s, poly(arylene ether ketone)s, poly(arylene ether sulfone), and polyimides [62-64] are regarded as promising candidates to Nafion due to their cost-effectiveness, easiness of polymer structure modification, and good mechanical, chemical, and thermal stability [65-68]. Sulfonated aromatic hydrocarbon polymers generally

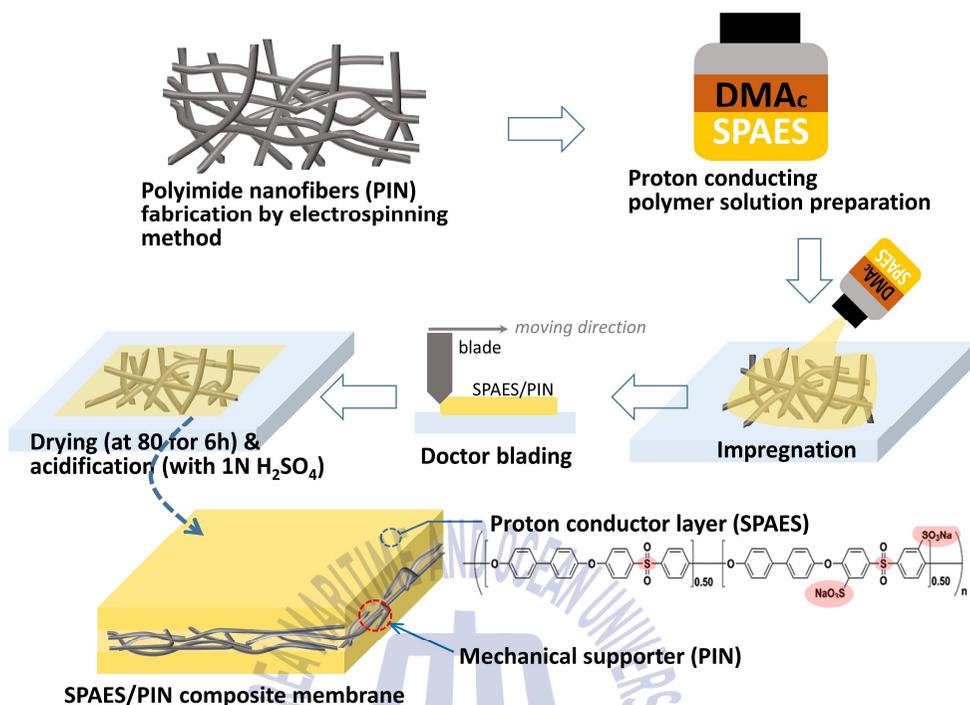
have high ion exchange capacity (IEC) and water uptake (WU); therefore, comparable proton conductivity could be achieved. However, this characteristic lead to negative consequences such as excessive swelling and deteriorate mechanical properties [69, 70].

In order to overcome the drawbacks of sulfonated aromatic hydrocarbon polymers, **Nakabayashi et al.** reported the method to synthesize highly sulfonated multiblock poly(ether sulfone)s with postsulfonation using concentrated sulfuric acid. The synthesized membranes have ion exchange capacity (2.75–2.79 mmol/g) which exhibits similar proton conductivity as Nafion 117. Suggesting that high proton conductivity is achieved by showing homogeneous formation of proton conductive channels through the AFM image [71]. In addition, **Pang et al.** developed poly(arylene ether)s with a high density sulfonated hexaphenyl pendant group which can control positions and the degree of sulfonation. The polymer thus developed showed excellent dimensional stability with lower water uptake. Membranes made from this polymer also have good proton conductivities and low methanol permeability. **Pang et al.** further introduced new fluorinated poly (arylene ether ketone) containing hexa sulfophenyl as a hydrophilic pendent group to increase the polarity difference of hydrophilic and hydrophobic parts. Due to the well-defined phase separation, membrane exhibited a low dimensional change value and high proton conductivity [72]. Also, **Wang et al.** presented a novel poly(ether sulfone) based on fluorene having two pendant phenyl substituents to provide a clustered pendant sulfonic acid group. The sulfonated polymers exhibited high oxidative and dimensional stabilities, despite clearly separating the ion domain of 3–7 nm in size [72, 73].

## Chapter 3. Materials and methods

### 3.1 Membrane preparation

For MEC application, a SPAES/PIN composite PEM was fabricated by impregnating PIN in the center of a SPAES polymer solution (Fig. 3.1). Thus, the newly developed composite membrane structure consists of a SPAES polymer layer that plays a role in proton transfer and a PIN substrate embedded as a supporter inside the polymer layer to enhance its mechanical strength and dimensional stability. The manufacturing method of the composite membrane is similar to that reported in our previous study [6], except that SPAES is used instead of SPEEK as a proton-conducting polymer. SPAES polymer solution was prepared using SPAES of  $>1.75$  meq/mg IEC, polymerized by Kolon (South Korea), and N,N-dimethylacetamide (DMAc) as a solvent. The degree of sulfonation (DS), incorporation of  $-\text{HSO}_3$  groups into polymer main chain, was 100%. As a supporting substrate for this composite membrane, PIN was selected due to its excellent mechanical properties and compatibility with SPAES polymer, and it was fabricated by the electrospinning method with an average fiber thickness of 200 nm. Finally, the composite membrane was prepared by pouring the SPAES/DMAc polymer solution onto the PIN substrate on a glass plate, followed by natural drying at  $80^\circ\text{C}$  for 6 h on a clean bench. The membranes were acidified in a 1 N boiling sulfuric acid solution for 2 h and washed with deionized water.



**Figure 3.1.** Fabrication procedure and concept of sulfonated poly(arylene ether sulfone)/polyimide nanofiber (SPAES/PIN) composite proton exchange membrane (PEM). The structure of ionomer was expressed using a representative example of SPAES.

## 3.2 Membrane property characterization

### 3.2.1 Morphology and mechanical property analysis

The morphology of the fabricated membrane was observed using a field emission scanning electron microscope (FE-SEM, TESCAN-MIRA 3 LMU, Czech), and its material composition was analyzed using energy-dispersive X-ray (EDX) spectroscopy. Atomic force microscopy (AFM) was used to observe the microphase separation of the SPAES/PIN

composite membrane. The AFM images were recorded in the soft tapping mode, which provides the surface topography along with the shape of the microdomains of different material properties, at room temperature. To evaluate the mechanical strength of membranes under the operational environment of the MEC, hydrated membrane samples were prepared and then the tensile strength was measured with an Instron 5967 tension tester (Instron Corp., USA) at room temperature. To minimize experimental errors, at least three specimens from each membrane sample (50 mm length  $\times$  20 mm width) were tested and averaged at a crosshead speed of 50 mm/min (ASTM D882).

### 3.2.2 Water uptake, swelling ratio, and ion exchange capacity measurement

WU was evaluated by examining the weight difference between the dry and wet membranes. Dry membranes were weighed after drying at 80°C in a dry oven until a certain value ( $W_{dry}$ ). To measure the wet weight of the membrane, the dry membranes were soaked in distilled water at room temperature (25°C) for 24 h and then weighed immediately after taking them out of the distilled water and removing surface water using an absorbent paper ( $W_{wet}$ ). The WU was estimated using equation (3) [74, 75]. The swelling ratio in area ( $\Delta A$ ) and thickness ( $\Delta T$ ), representing the difference in the dimensions before and after hydration of the membrane, were also measured using equations (4) and (5), as previously described [6]:

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (3)$$

$$\Delta A(\%) = \frac{A_{wet} - A_{dry}}{A_{dry}} \times 100 \quad (4)$$

$$\Delta T(\%) = \frac{T_{wet} - T_{dry}}{T_{dry}} \times 100 \quad (5)$$

The IEC of the membranes was evaluated using the typical titration method described in a previous study [15]. To accomplish this, square-cut membranes (2 cm × 2 cm, acid form) were immersed in 20 mL of 1 M NaCl solution for 24 h to substitute sodium ions for protons in the membranes. Then, the released protons from the membranes were titrated using a 0.1 M NaOH solution with a phenolphthalein indicator. The IEC was calculated according to equation (6) [76–78]:

$$IEC \text{ (meq/g)} = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \quad (6)$$

where  $V_{NaOH}$  is the consumed volume of NaOH solution (mL) and  $C_{NaOH}$  is the molar concentration of NaOH solution (mol/L). All experiments were conducted in quadruplicate to reduce measuring errors.

### 3.2.3 Ion conductivity: proton transport number measurement

To calculate the proton transport number ( $\bar{t}_+$ ) of the membranes, a two-chambered measuring cell, separated by the membrane, with a Luggin capillary containing a Ag/AgCl reference electrode (+0.195 V vs. NHE; Microelectrode, USA) was used as described in previous study [79]. The membrane specimens were snipped at a small size (2 cm × 2 cm) and soaked in 0.01N HCl solution for a day. Then, the prepared

membrane was sandwiched between the chambers, and each chamber was filled with 0.01 N ( $C_1$ ) and 0.05 N ( $C_2$ ) HCl solution. Following this, the potential difference ( $E_m$ , mV) between the two chambers was measured using a multimeter (2700 Data Acquisition Series, Keithley, USA) at 2 s intervals [80] to calculate the transport number using the following equation:

$$\bar{t}_+ = \frac{\left\{ \frac{E_m \cdot F}{R \cdot T \cdot \ln\left(\frac{C_1}{C_2}\right)} + 1 \right\}}{2} \quad (7)$$

where  $F$  is the Faraday constant (96485.3 C/mol),  $R$  is the ideal gas constant (8.314 J/K · mol), and  $T$  is the absolute temperature (K).

### 3.3 Crossover measurement for the cation, substrate, and gas

A three-chambered cell was designed to compare the permeability of cations, substrates, and gases for Nafion-211 and the developed membrane, as shown in Fig. 3.2a. This cell consisted of a central anode chamber (180 mL) and two adjacent cathode chambers (180 mL working volume each) located on either side of the anode chamber, and test membranes (Nafion-211 and SPAES/PIN composite membrane; 5 cm × 5 cm) were inserted between the anode and cathode chambers.

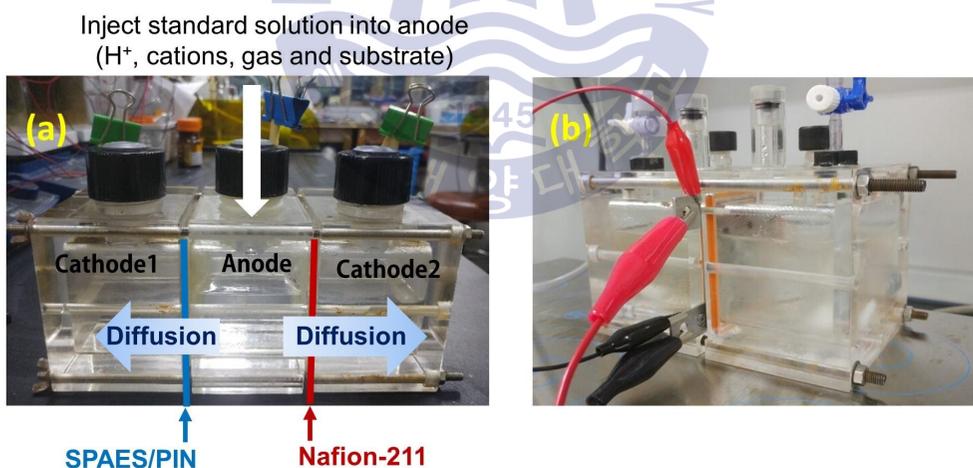
For cation crossover measurement, standard solution containing multiple cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in 100 mg/L) was filled into the only anode chamber, while filling distilled water into two cathode chambers. After that, cations that were diffused from the anode to the cathode through the membranes over time by the concentration gradient

were measured using ion chromatography (ICS5000, DIONEX, USA). For the substrate diffusion test, acetate was injected into the only anode chamber at a concentration of 1,000 mg/L, and its diffusivity was measured in a similar way using high-performance liquid chromatography. For gas crossover analysis, all three chambers of the cell were filled with distilled water at half of the volume for the prevention of membrane drying, and the headspace was flushed with nitrogen gas. Following this, standard gas (5% H<sub>2</sub>, 70% CH<sub>4</sub>, and 25% CO<sub>2</sub>, in % volume per volume) was filled into the anode chamber, and gas diffusion through the membrane was observed using a gas chromatograph (Series 580, GawMac Instrument Co., USA) equipped with a thermal conductivity detector and a Porapak Q sieve column with nitrogen gas (99.999%) as a carrier gas. All mass transfer experiments were conducted in an uninoculated cell at a constant temperature of 25±1°C unless otherwise stated.

### **3.4 Evaluation of actual membrane performance using a hydrogen-producing microbial electrolysis cell (MEC)**

After intensive investigation of the membrane properties using an uninoculated test cell, to compare their actual performance in a real environment, the SPAES/PIN composite membrane and Nafion-211 (as a control) were applied to hydrogen-producing two-chambered MECs (180 mL working volume each), which were operated in a fed-batch mode for over 6 months at 25±1°C following previous studies [1, 81]. In the MECs, the anode for exoelectrogen enrichment was carbon felt (25 cm<sup>2</sup>) and the cathode was a Pt-loaded perforated titanium plate (0.5mg Pt/cm<sup>2</sup>) of the same size as the anode. A nutrient mineral buffer (pH

7.0) was used as the anolyte to support anodic bacterial growth, while phosphate-buffered solution (pH 7.0) was employed as the catholyte, and acetate (3mM) was used as a substrate. To initiate hydrogen production, a voltage of 0.5 V was applied to the MECs using a DC power supply. For gas production and composition analysis, gas samples (1.0 mL) were taken from the headspace of the MECs using a gastight syringe (2.5 mL, Hamilton SampleLock syringe #1002, USA) and analyzed using a gas chromatograph (Series 580, GawMac instrument Co., USA) equipped with a thermal conductivity detector and a Porapak Q sieve column, with nitrogen gas (99.999%) as the carrier gas. To evaluate the actual performance of the membranes, the hydrogen generation efficiencies were compared using the MECs equipped with the test membranes (Nafion vs. SPASE/PIN) after 3 months of prestabilization.



**Figure 3.2.** Photograph of (a) the three-chambered cell for mass transfer analysis and (b) the two-chambered hydrogen-producing microbial electrolysis cell (MEC).

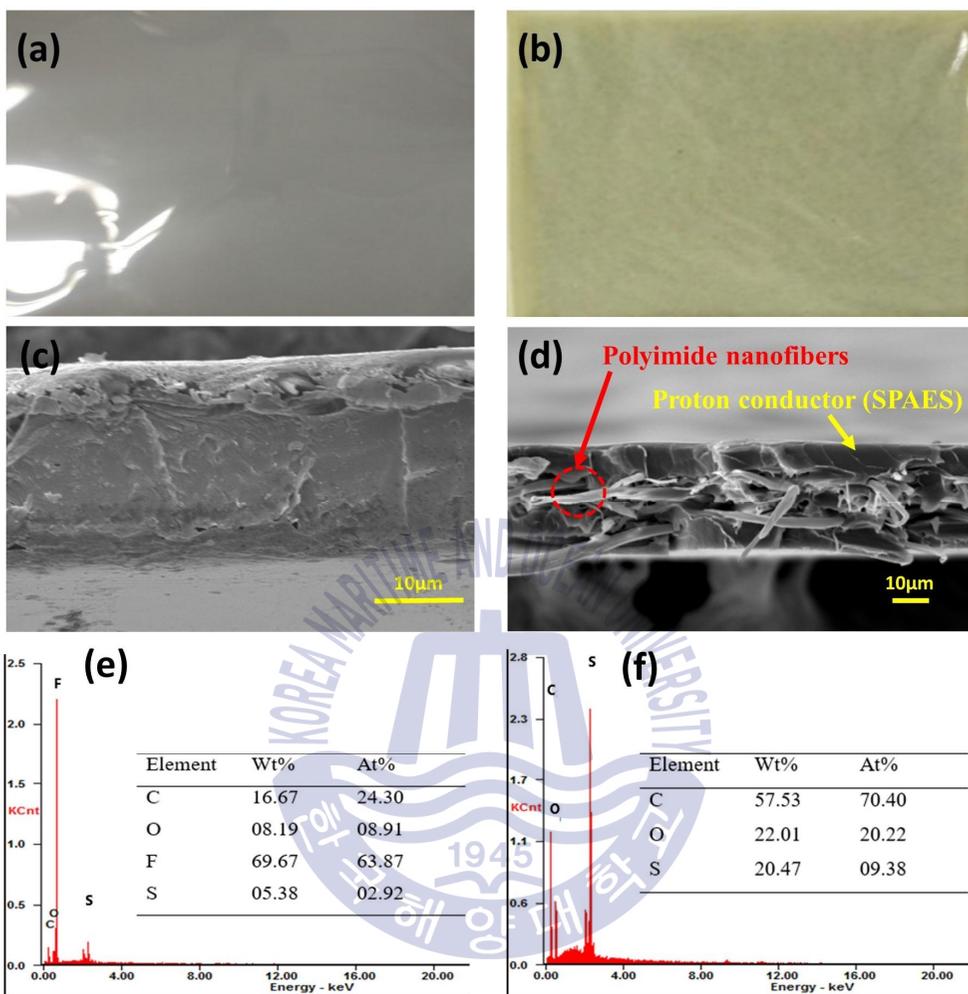
## Chapter 4. Results and discussion

### 4.1 Water uptake, tensile strength, swelling ratio, and ion exchange capacity

Table 1 represents the basic properties of the tested membranes, such as WU, tensile strength, swelling ratio, and ion exchange capacity. The newly developed SPAES/PIN composite membranes showed better performance in terms of mechanical stability and higher IEC than the Nafion-211 membrane with a similar thickness did (Table 1). As shown in the SEM image in Fig. 4.1, the SPAES/PIN membrane was well fabricated based on its manufacturing concept. This composite membrane was ultrathin, with a  $21 \pm 2 \mu\text{m}$  thickness, and the support nanofibers (PINs) were evenly embedded in the center of the SPAES proton-conducting polymer matrix, as intended. Based on published works [9, 82], polyvinylidene fluoride (PVDF) and poly(tetrafluoroethylene) (PTFE) are the membrane substrates that are most commonly used to enhance mechanical properties. However, PTFE is hydrophobic; thus, it exhibits weak compatibility with other PEMs. However, the nanofibers, which were as thin as 200 nm, showed high compatibility with the SPAES polymer, enabling close adhesion at the interface between SPAES and the nanofibers. The compatibility of materials is an important factor for composite membrane fabrication because the higher the compatibility, the better the mechanical stability and durability. The nanofibers used in this study were much thinner than those used in our previous research [6], which already demonstrated a successful contribution of PINs to improving the mechanical strength of the membrane without losing proton conductivity, thereby enhancing the impregnation efficiency of the SPAES solution.

According to the EDX results showing relative atomic percentages (Fig. 4.1e, f), the fluorine content (63.87 atomic %) was the highest in the Nafion-211 membrane due to its fluorocarbon backbone, whereas the composite membrane showed the highest carbon content (70.4%), clearly indicating its hydrocarbon-based polymeric characteristics. Specifically, the SPAES/PIN composite membrane exhibited 3.2 times higher sulfur content than Nafion-211 did, implying a correspondingly greater presence of the sulfonated ion clusters ( $\text{SO}_3\text{H}$  groups) responsible for proton transfer in the cation exchange membrane.

According to many previous studies [75, 76, 83, 84], a high WU rate of the membrane can lead to high proton conductivity because sorbed water molecules play a role as a proton-transporting medium in the hydrophilic regions of the membrane; however, WU that is too high can have the adverse effect of excessive membrane swelling or mechanical instability [6]. The SPAES/PIN composite membrane showed about 3-fold higher WU ( $35 \pm 3\%$ ) compared to the Nafion-211 membrane ( $10 \pm 4\%$ ), exhibiting a similar difference in the IEC ( $2.3 \pm 0.3$  meq/g for SPAES/PIN vs.  $1 \pm 0.2$  meq/g for Nafion-211). Nevertheless, membrane swelling problems commonly occurring in hydrocarbon-based polymers, such as SPAES and SPEEK, due to their excessive WU did not occur in the developed membranes. This high resistance to swelling (3.0 times greater in the areal direction than Nafion-211) can be explained by the fact that the embedded supporting nanofibers efficiently suppressed the expansion of the polymer matrix by holding tightly. In addition to this high dimensional stability, the SPAES/PIN composite membrane showed a stronger tensile strength of over 40 MPa—compared to 23 MPa for Nafion-211—due to membrane reinforcement with nanofibers. Overall, these improvements indicate that the fabricated composite membrane has excellent potential for fuel cell or MEC applications.



**Figure 4.1.** Photographs for (a) Nafion-211 and (b) the SPAES/PIN composite membrane; SEM images showing a cross-sectional view of (c) Nafion-211 and (d) the SPAES/PIN composite membrane; EDX spectra for (e) Nafion-211 and (f) the SPAES/PIN composite membrane.

**Table 4.1.** Physicochemical properties and mechanical properties of the SPAES/PIN composite membrane and Nafion-211.

Membrane	Thick- ness ( $\mu\text{m}$ )	WU (%)	Area swelling ratio (%)	Thickness swelling ratio (%)	Tensile strength (MPa)	IEC (meq/g)	DS (%)	Proton conductivity (S/cm)
SPAES/ PIN	$21 \pm 2$	$35 \pm 3$	$7.5 \pm 0.5$	$19.0 \pm 1$	>40	$2.3 \pm 0.3$	100	$0.17 - 0.2$
Nafion- 211	$25 \pm 1$	$10 \pm 4$	$22.4 \pm 0.5$	$22.4 \pm 1$	23	$1 \pm 0.2$	n/a	n/a

Data indicate the mean  $\pm$  standard deviation (n=4).

not only the SPAES polymer but also the support, so the IEC value is less than that of the pure SPAES polymer. b The ionomer was prepared by postsulfonation on predesignated site of hydrophilic unit and the whole hydrophilic sites were proven to be sulfonated by NMR spectroscopy. c The proton conductivity was measured at 80°C and 95% relative humidity. SPAES = sulfonated poly(arylene ether sulfone), PIN = polyimide nanofiber.

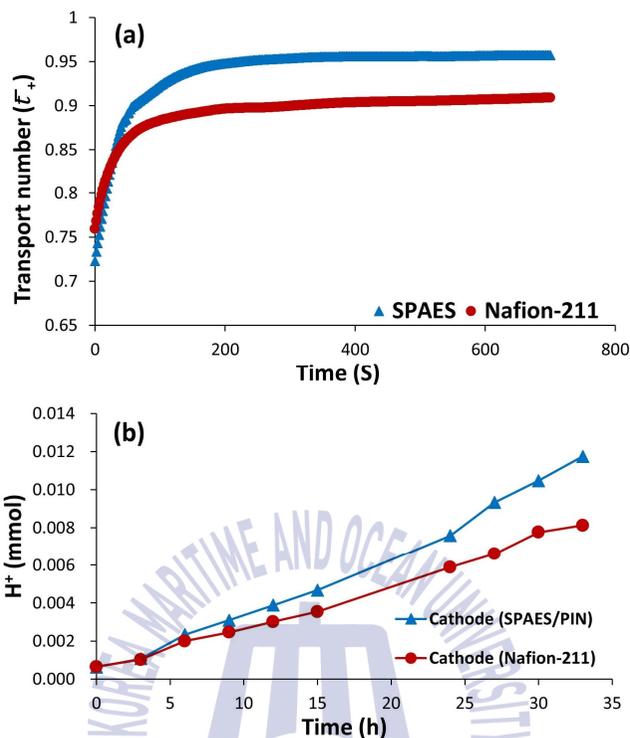
#### 4.2 Proton selectivity

Due to the cations supplied for microbial growth in the MECs, various cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , etc.) were present at enormously higher concentrations (typically 105 times) in the anode chamber than the protons ( $\text{H}^+$ ) were [2, 7]. These cations also have high affinity for negatively charged sulfonic acid ( $-\text{HSO}_3$ ) clusters, which are proton-conducting channels in PEMs; thus, they compete with protons for those clusters [18, 80, 83]. Such competition causes severe pH gradient development across the PEM (lower pH at the anode and higher pH at the cathode in the MECs) due to retarded proton transport from

the anode to cathode. A pH decrease in the anode inhibits the activity of exoelectrogens, subsequently causing a serious MEC performance drop. Therefore, proton selectivity, which selectively transfers protons while excluding other competitive cations, is a more important requirement for the PEM of MECs where complex cations coexist with protons than simply the proton conductivity, which was traditionally emphasized in the field of PEMs. To evaluate how the membrane selectively transported protons, the membrane's proton transport number and the cation's crossover tendency were analyzed.

#### 4.2.1 Ion conductivity: proton transport number

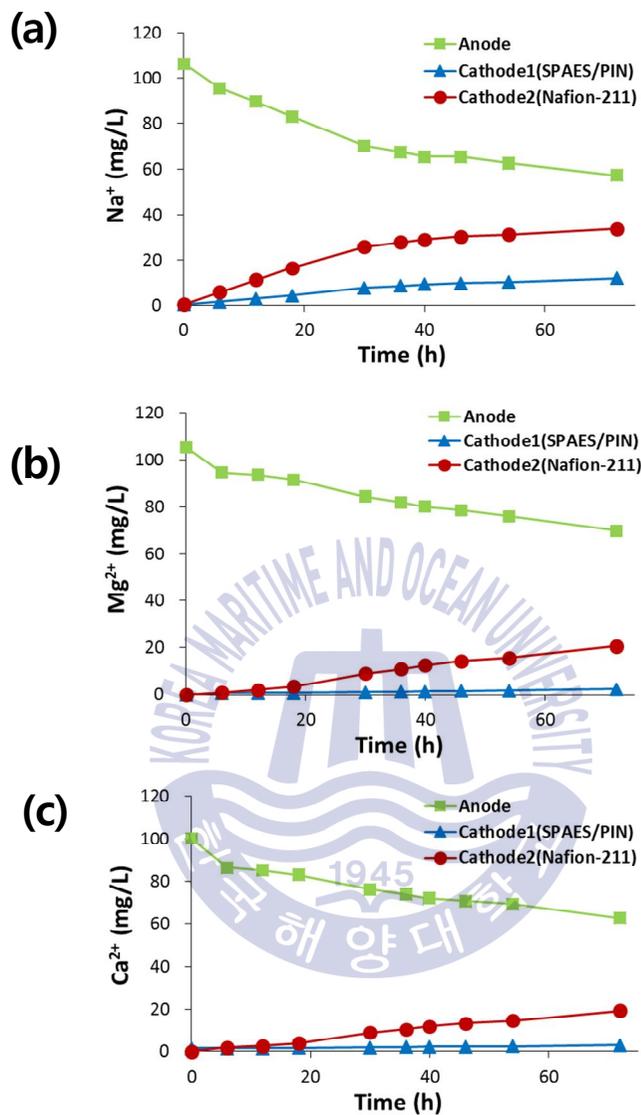
The proton transport number ( $\bar{t}_+$ ) of the SPAES/PIN composite membrane was 0.96, as measured with hydrochloric acid, which was higher than the 0.91 of Nafion-211; this indicated a correspondingly greater capability of the composite membrane's proton transportability (Fig. 4.2a). In addition, when the diffused amount of protons was measured using a three-chambered cell, the SPAES/PIN composite PEM showed a 1.5-fold faster proton transfer than Nafion-211 did (Fig. 4.2b). The proton conductivity of the SPAES/PIN membrane was 0.17–0.2 S/cm, as determined with a two-probe electrochemical impedance spectroscopy.



**Figure 4.2.** Electrochemical properties comparisons (SPAES/PIN membrane vs. Nafion-211): (a) proton transport number, (b) proton diffusion through membranes.

#### 4.2.2 Competitive cation crossover

For cation crossover testing using a the three-chambered cell, the anode chamber was filled with a solution containing 100 mg/L of  $Na^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$ , and then the amount of diffused cations into cathode chambers containing distilled water through both test membranes was determined over time. During this test, the amount of cations decreasing at the anode precisely matched with the amount delivered to the two cathode chambers through the membranes without any unknown losses.



**Figure 4.3.** Cation crossover comparisons between the SPAES/PIN composite membrane and a Nafion-211 membrane: (a) sodium ion, (b) magnesium ion, (c) calcium ion.

All tested cations were found to be diffused through both membranes, but the SPAES/PIN composite membrane was significantly less permeable

to those cations than Nafion-211 (Fig. 4.3), exhibiting 3–10-fold lower cation crossover depending on the cation species. Of the tested cation species, the monovalent sodium ions diffused more easily than divalent cations despite their smaller ionic charge. This is probably because, compared to divalent cations, sodium ions can more easily combine with  $\text{SO}_3^-$  in the sulfonic acid groups in PEMs, as both are monovalent; thus, monovalent cations on the sulfonic acid ( $-\text{HSO}_3$ ) groups hop more favorably from one acid side to another. In particular, the SPAES/PIN membrane showed substantially lower permeability for divalent cations ( $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) compared to Nafion-211.

#### 4.2.3 High proton selectivity based on microphase separation

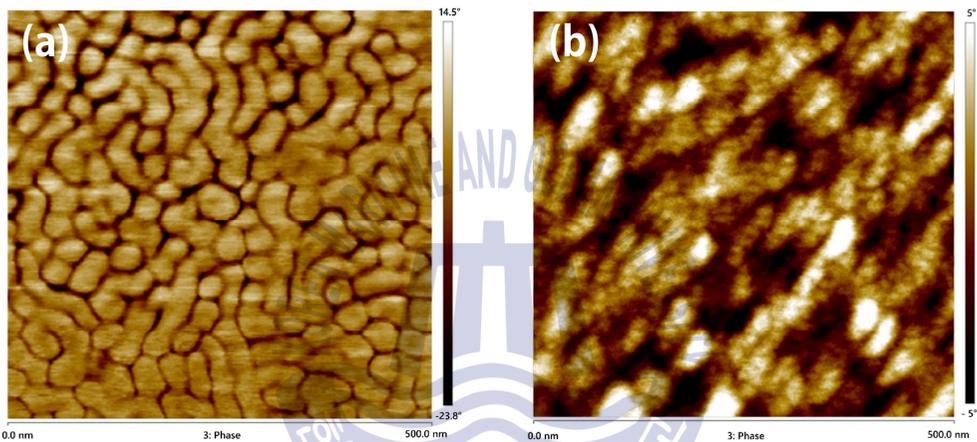
Compared to Nafion-211, the SPAES/PIN composite membrane showed not only improved proton conductivity but also selectivity; it exhibited a relatively greater affinity for protons but less affinity for other competitive cations (Figs. 4.2 and 4.3). This unique feature makes this membrane suitable for application to real MECs in which various cations coexist with protons, as the pH gradient across the membrane causing performance deterioration can be mitigated due to the selective transfer of protons from anode to cathode.

Although no model has yet been identified as fully correct, this feature could be explained by the microstructural difference of SPAES proton-conducting polymer compared to Nafion-211. In general, PEMs have a microphase separated morphology of discrete hydrophobic (i.e., backbone) and hydrophilic cluster (i.e., ion conducting site) regions [8, 85], as the constitutive components of block copolymers tend to phase separate into chemically homogenous domains. As compared with

fluorocarbon-based Nafion-211, hydrocarbon-based polymers like SPAES have a more even distribution of hydrophobic or hydrophilic clusters because the aromatic rings of their backbones are more hydrophilic (Fig. 4.4). This results in a well-defined microstructure being formed, with narrower, more branched, more tortuous ion-conducting hydrophilic channels [6, 85, 86]. Therefore, cations with a size greater than that of the protons have relatively difficulty in passing through the channels formed across the SPAES membrane, indicating the membrane's enhanced selectivity for the protons.

So far, the investigation of alternate PEMs to improve proton conductivity and mechanical properties have mainly focused on the modification of SPAES and SPEEK by applying doping and blending, developing composites, and pretreatment. Tominaga and Maki [87] demonstrated that the introduction of sulfonated mesoporous organosilicate (s-MPO) into polybenzimidazole-doped composite membrane improved proton conductivity because s-MPOs have an ordered structure and many SO<sub>3</sub>H groups. Moreover, Kwon et al. [88] modified the SPAES side chain with hydroxyl side groups contributing additional hydrogen bonding; thus, the interconnected hydrophilic clusters and the extent of hydrophobic-hydrophilic microphase separation were enhanced. The overall performance improvement of SPEEK-modified membrane was reported when n-BuOH was introduced into the SPEEK to induce self-organization. This led to the formation of multiple hydrogen bonds between n-BuOH and SPEEK; thus, enhanced clustering of hydrophilic domains was formed in the SPEEK microstructure, resulting in improved proton conductivity [89]. Recently, Park et al. [90] developed a new concept of hydrocarbon-based PEMs, a nanocrack-regulated self-humidifying membrane, by depositing thin nanocracked hydrophobic

layers via plasma treatment. The nanocracks play as nanoscale valves to regulate water content and ion conductivity, thus improving electrochemical performance. According to the latest findings, the properties of our developed SPAES/PIN composite membrane could be further improved through the optimization of proton transport channels in SPAES polymer.



**Figure 4.4.** Microphase separation of (a) the SPAES/PIN composite membrane and (b) Nafion membrane observed by atomic force microscopy (AFM) in a tapping mode (dark=hydrophilic regions, bright=hydrophobic regions).

### 4.3 Gas and substrate crossover

In the anode of MECs, carbon dioxide is produced from substrate degradation by exoelectrogens, but methane and other gases are also commonly observed because the substrate and the anodic growth conditions are also favorable to methanogens. Therefore, in the case of MECs for producing high value-added chemicals (e.g., hydrogen, hydrogen peroxide, butanol, etc.), mixing of anode and cathode gases must be avoided to maintain high purity of the products. For this, a PEM can be inserted to prevent cross-contamination between anode gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$  etc.) and cathode gas ( $\text{H}_2$ ) [78, 81].

As shown in Fig. 4.5, the SPAES/PIN composite membrane was less permeable to all tested gases compared to Nafion-211: It was 2.7-fold less permeable for hydrogen gas and twofold less permeable for methane gas. Gas crossover through PEMs is an unavoidable problem in the MEC operation, so the relatively low gas permeability of the SPAES/PIN membrane can increase its practical applicability. As another problem associated with conventional PEMs, significant substrate leakage has been pointed out, which decreases the MEC performance due to the loss of available electron donors for exoelectrogens. Similar to the gas crossover results, the SPAES/PIN membrane exhibited reduced substrate permeability (Fig. 4.5c). These better resistances to gas or substrate crossover of our developed membrane could be also explained via the same characteristics as the microphase structural features that were described in terms of the cations' lower permeability (section 3.2.3).

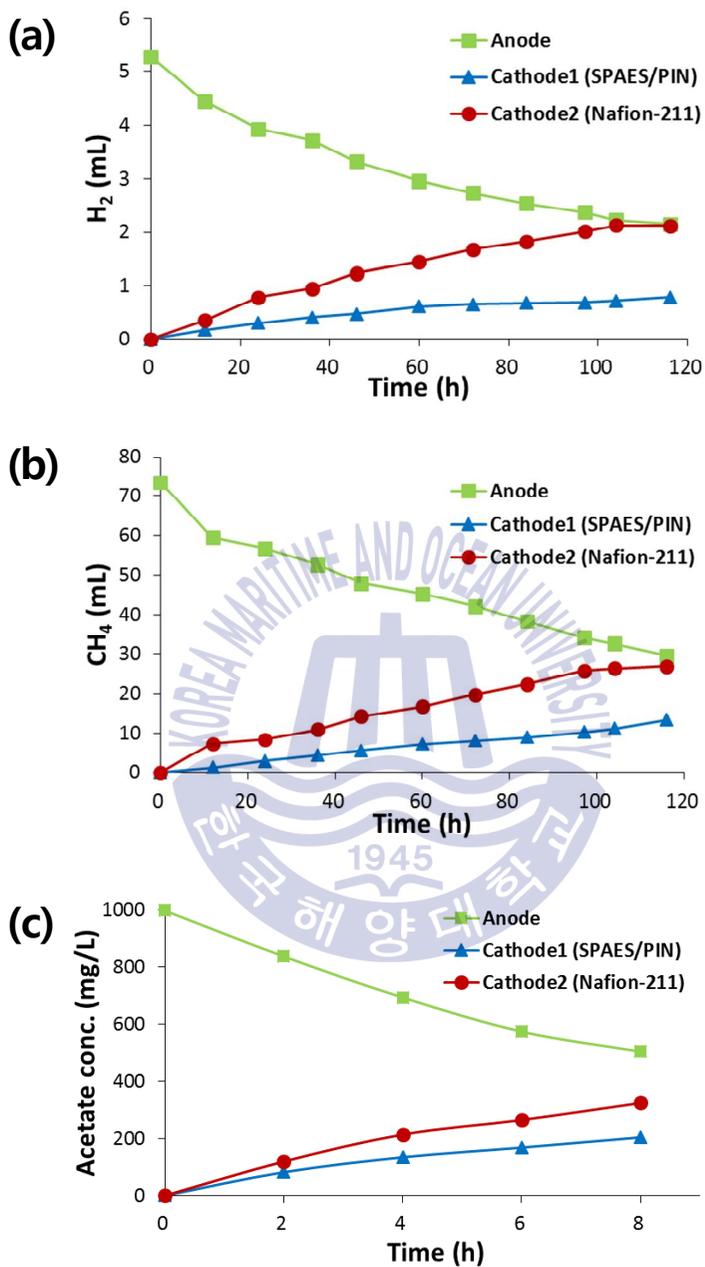


Figure 4.5. Gas and substrate crossover comparisons between a SPAES/PIN composite membrane and a Nafion-211 membrane: (a) hydrogen gas, (b) methane gas, (c) acetic acid.

#### 4.4 Actual performance verification using MECs

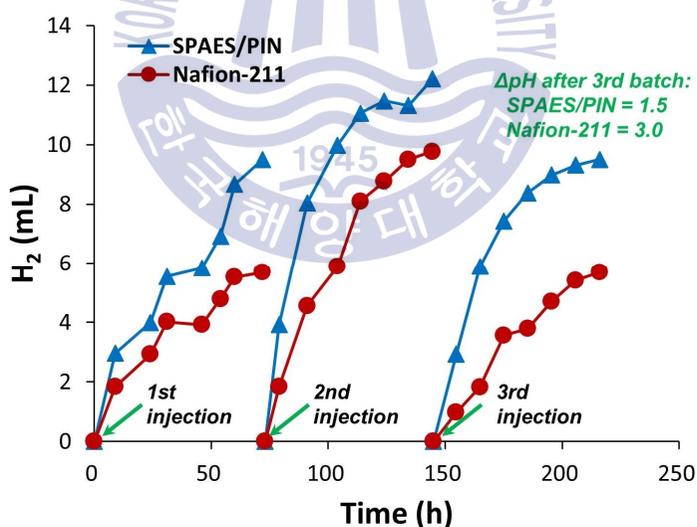
Figure 4.6 represents the actual hydrogen gas production of the MECs equipped with test membranes during a three-consecutive-feeding cycle without electrolyte replacement. The SPAES/PIN membrane showed not only significantly greater production of hydrogen gas but also higher hydrogen purity, compared to Nafion-211 (Fig. 4.6 and 4.7). When the SPAES/PIN membrane was applied, the overall hydrogen production efficiency was 32.4% higher than that of Nafion-211 (Fig. 4.6). As explained in our former study [6], the greater efficiency of the SPAES/PIN membrane was mainly attributed to the relatively greater proton selectivity of the membrane, which mitigated the accumulation of protons at the anode so that the pH gradient across the membrane was not formed at severe levels. In contrast, Nafion-211 caused a twofold higher pH gradient ( $\Delta \text{pH}=3.0$ ) than that of the SPAES/PIN composite membrane ( $\Delta \text{pH}=1.5$ ). The pH gradient leads to a performance reduction because a unit change in pH contributes to a potential loss of 0.06V. Therefore, the pH gradient of 3.0 occurring in Nafion-211 corresponded to a 0.18V loss of the applied voltage (0.5V), indicating a significant loss of driving force to initiate hydrogen production. After three consecutive feedings without the replacement of electrolyte solution, the pH of the anode chamber decreased from the initial 6.96 to 6.23 for the SPAES/PIN membrane, while it decreased from 7.04 to 5.52 for Nafion-211. In contrast, the cathode pH increased slightly from 7.01 to 7.71 for SPAES/PIN membrane but increased significantly from 7.01 to 8.44 for Nafion-211 due to delayed proton transfer. A severe anodic pH decrease is especially harmful for exoelectrogens, and this resulted in the corresponding reduction of hydrogen production when Nafion-211 was used. Another reason for the greater efficiency of the SPAES/PIN

membrane was its lower loss of produced hydrogen, as well as the minimized substrate crossover through the membrane due to membrane's low permeability. With regard to the increased hydrogen production as the SPAES membrane was employed compared to Nafion membrane, the improved proton selectivity of the membrane mainly contributed to 69.5% of increased hydrogen production, while the decreased crossover of gases and substrate across membrane just accounted for a relatively little portion of 11.7% and 18.8% of the hydrogen gas increment, respectively.

The high purity of produced hydrogen gas is another advantage of two-chambered MECs applying a membrane. Figure 4.7 represents the gas composition under the condition that the methanogens are also growing competitively with the exoelectrogens in the anode, showing a relatively higher methane content than that of the typical MEC operating conditions. In the case of the SPAES/PIN composite membrane, the gas produced at the cathode consisted of mainly hydrogen (90.3%) with minor impurities of methane 6.37% and carbon dioxide 3.30% diffused from the anode. In contrast, Nafion-211 showed significantly lower hydrogen content of 61.8%, with a large portion of undesirable gases diffused from the anode ( $\text{CO}_2$  21.3% and  $\text{CH}_4$  16.9%). When methanogens were suppressed in the anode using a specific inhibitor, 2-bromoethansulfonate, almost 97.2% hydrogen purity was achieved for the SPAES/PIN membrane.

In terms of proton transport, membraneless systems are more favorable due to the elimination of membrane-associated resistance [77, 91-93], but this merit is diminished because they contaminate value-added products (e.g., hydrogen gas) with undesirable gases diffused from the anode. As compared to Nafion-211, the newly developed

hydrocarbon-based SPAES/PIN composite membrane showed overall performance improvement in relation to proton selectivity, gas and substrate crossover, and mechanical stability. According to the results of electrochemical impedance spectroscopy test for the internal resistance measurement, the MEC equipped with the SPAES/PIN membrane showed lower internal resistance by  $49.5 \Omega$  than that of Nafion-211, due to the membrane's excellent proton selectivity. In particular, employing PINs as a supporter in SPAES polymer did not cause any sacrifice of proton conductivity, although PINs are inactive for proton transport. Therefore, this membrane can be suitably used for MECs as an alternative PEM to the Nafion membrane, and it can potentially be applied in diverse areas requiring PEMs, such as fuel cells, reverse electro dialysis cells, the chlor-alkyl industry, and gas separation.



**Figure 4.6.** Comparison of hydrogen gas production between the microbial electrolysis cells (MEC) equipped with the SPAES/PIN composite membrane and a Nafion-211. Arrows indicate acetate injection as a carbon source for producing hydrogen gas.

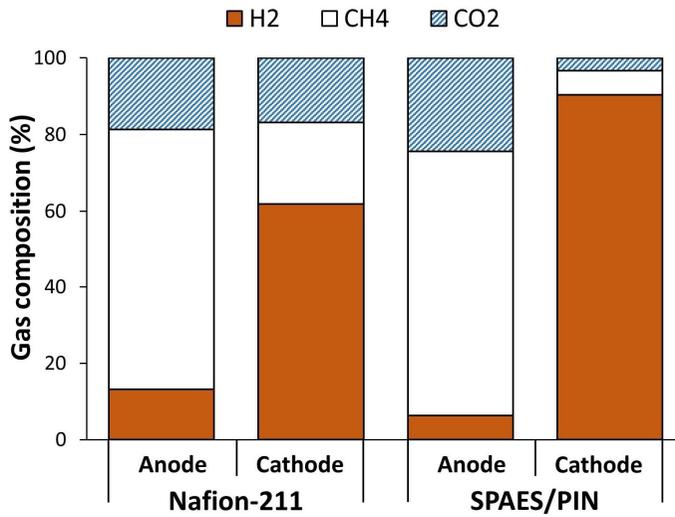


Figure 4.7. Gas composition comparisons between a SPAES/PIN composite membrane and Nafion-211.



## Chapter 5. Conclusion

A SPAES/PIN composite PEM, a new type of non-fluorine membrane, was developed and applied for hydrogen-producing MECs. The SPAES had greater proton selectivity due to its excellent microphase separation, allowing for more even and narrower proton-transporting channels in the membrane. PINs were well embedded in the SPAES polymer matrix without sacrificing proton conductivity, and they could efficiently reinforce the composite membrane due to their high compatibility with the SPAES. As compared with Nafion-211, the SPAES/PIN composite membrane showed significantly better performance in terms of proton transport, mechanical strength, and gas or substrate crossover. Above all, this novel membrane exhibited significantly enhanced selective transport of protons while excluding other competing cations, which reduced the extent of pH gradient across the membrane; thus, improved hydrogen production was observed when the membrane was applied to actual MECs. Therefore, this newly developed SPAES/PIN composite membrane is considered as a promising material for PEMs, especially for use where protons and other competing cations are present together like in MECs, due to its superior proton selectivity. The unique features of the SPAES/PIN membrane make it suitable for a broad range of applications in diverse areas requiring PEMs, such as fuel cells, reverse electrodialysis cells, the chlor-alkyl industry, and gas separation.

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## Academic achievement

### Peer-reviewed journal article (International)

1. **S.G. Park**, K.J. Chae, M. Lee, A sulfonated poly(arylene ether sulfone)/polyimide nanofiber composite proton exchange membrane for microbial electrolysis cell application under the coexistence of diverse competitive cations and protons, *Journal of Membrane Science*, 540 (2017) 165–173. (IF = 6.035)

### Conference presentations (International)

1. **Sung-Gwan Park**, Wan-Cheol Cho, Kyu-Jung Chae, Methanogen activity control with 2-bromoethanesulfonate (BES) and coenzyme M in microbial electrolysis cell for the production of electrobiofuels, *The 15th IWA world conference on Anaerobic Digestion*, Beijing, China, 17-20 Oct, 2017, p.71
2. Eun-Bi Son, **Sung-Gwan Park**, Kyung-Min Poo, Jae-Soo Chang, In-Soo Kim, Kyu-Jung Chae, Magnetic biochar and Chitosan revised-magnetic biochar derived from marine algae for heavy metals (Cd, Cu and Zn) removal, *2017 International Environmental Engineering Conference*, Jeju, Republic of Korea, 15-17 Nov, 2017, p.742-743
3. Kyeong-Rok Kim, **Sung-Gwan Park**, Kyung-Min Poo, Kyu-Jung Chae, Electromethanogenesis using metal nanoparticle-activated carbon composite, *ABBS 2016*, Jeju, Republic of Korea, 5-8 Oct, 2016, p.138-139
4. **Sung-Gwan Park**, Moo-Suk Lee, Kyung-Rok Kim, Kyu-Jung Chae, Sulfonated poly(arylene ether sulfone)-based composite proton exchange membrane for electrobiofuel production, *The 3rd AP-ISMET*, Busan, Republic of Korea, 31 Aug-2 Sep, 2016, p.130

## Conference presentations (Domestic)

1. **박성관**, 김경록, 김인수, 채규정, 미생물 전기분해 반응조(MEC)에서 2-Bromoethanesulfonate (BES)와 Coenzyme M을 이용한 메탄과 수소의 생성 조절, *2017 대한환경공학회 국내학술대회*, 제주, 대한민국, 15-17 Nov, 2017, p.266-267
2. 조완철, **박성관**, 김태남, 부경민, 채규정, 복합촉매 DSA 전극을 이용한 유류폐수의 전기화학과도산화 처리, *2017 한국물환경학회*, 광주, 대한민국, 23-24 Mar, 2017, p.755-756
3. **박성관**, 이무석, 김경록, 부경민, 채규정, Sulfonated poly(arylene ether sulfone)(SPAES) 이온 전도체를 이용한 탄화수소계 양이온 교환막의 MEC에 대한 적용 가능성 평가, *2016 대한환경공학회 국내학술대회*, 경주, 대한민국, 16-18 Nov, 2016, p.217-218

## Patent

1. 채규정, 부경민, **박성관**, 조완철, 압력조절식 미세기포 가압부상분리 장치와 이를 이용하는 가압부상분리 방법 및 이들을 이용하는 수처리 시스템, 출원번호: 10-2017-0017296, 02 Aug, 2017