



# 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



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## ARTICLE INFO

### Keywords:

Hydrogen gas  
Ion cluster channel  
Microbial electrolysis cells  
Proton exchange membrane  
Sulfonated poly(arylene ether sulfone)

## ABSTRACT

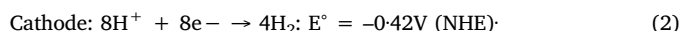
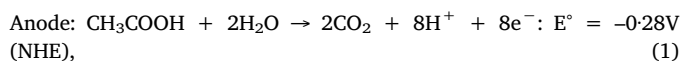
A sulfonated poly(arylene ether sulfone) (SPAES)/polyimide nanofiber (PIN) composite proton exchange membrane was developed for use in microbial electrolysis cells (MECs), where diverse cations that compete with proton coexist in high concentrations. It was fabricated by impregnating SPAES as a proton-conducting 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.

## 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 Eqs. (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 ( $CO_2$ ,  $CO$ ,  $CH_4$ , 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

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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  $10^5$  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 ( $\text{CO}_2$ ,  $\text{CH}_4$ , 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 ( $-\text{CF}_2-\text{CF}_2-$ ) and hydrophilic side chains with sulfonic functional groups ( $-\text{HSO}_3$ ) [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.

## 2. Materials and methods

### 2.1. Membrane preparation

For MEC application, a SPAES/PIN composite PEM was fabricated by impregnating PIN in the center of a SPAES polymer solution (Fig. 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 °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.

### 2.2. Membrane property characterization

#### 2.2.1. 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

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