Sulfonated polyether ether ketone (SPEEK)-based composite proton exchange membrane reinforced with nanofibers for microbial electrolysis cells

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HIGHLIGHTS

- A new type of composite proton exchange membrane was developed.
- Sulfonated polyether ether ketone was used as a proton conductor.
- Nanofibers were embedded in the proton conducting polymer matrix as a supporter.
- This novel membrane showed promising advantages over Nafion on performance.
- It improved hydrogen gas production as used for microbial electrolysis cells.

ABSTRACT

A nanofiber-reinforced composite proton exchange membrane (NFR-PEM), based on sulfonated polyether ether ketone (SPEEK) as a proton conductor, was prepared and studied for microbial electrolysis cells (MECs). The poor dimensional stability of conventional SPEEK membrane was overcome by embedding a polyimide nanofiber substrate in the centre of the polymer matrix, without sacrificing proton conductivity. This novel membrane showed lower gas and fuel crossovers, with higher proton conductivity, compared to a Nafion membrane. The installation of NFR-PEM into MECs improved hydrogen gas production at the cathode, with an overall hydrogen efficiency ($\eta$) of 86.4 $\pm$ 14.7%, as compared to 77.2 $\pm$ 10.3% of Nafion. In particular, higher proton selectivity of the NFR-PEM remarkably mitigated the anodic pH decrease harmful for anode bacteria, by facilitating selective proton transfer rather than other competing cations, which led to overall improved hydrogen gas yield in the MEC as the NFR-PEM was installed.

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1. Introduction

Recent advances in microbial fuel cell (MFC)-based technology, including a microbial electrolysis cell (MEC), have highlighted its potential as a water and energy nexus solution [1–3]. Instead of electricity generation of MFC, the MEC produces hydrogen gas, as shown in two half reactions indicated below (Eqs. (1) and (2)). Much effort is still needed before MFC-based technologies can become a cost-effective method. The major problems related to their practical application, efficiency of extracting electric energy and relatively high cost of such cells, could be resolved with the invention of a novel material, such as a proton exchange membrane (PEM), and its use inside the cells [4–6]. A PEM is an important component in MFC-based technology, and its essential function is separation of reactants and transport of protons from anode to cathode. A PEM is a semipermeable membrane generally made from ionomers, and designed to conduct protons, while being impermeable to gases such as oxygen and hydrogen. PEMs can be made from either pure polymer membranes, or from

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composite membranes, where other materials are embedded in a polymer matrix [7–11].

Anode : \( \text{CH}_2\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- : E^0 = -0.282\text{V(NHE)} \) (1)

Cathode : \( 8\text{H}^+ + 8\text{e}^- \rightarrow 4\text{H}_2 : E^0 = -0.422\text{V(NHE)} \) (2)

The most common PEM material is Nafion (DuPont, US) that has a hydrophobic Teflon-like backbone (\(-\text{CF}_2-\text{CF}_2-)\), with hydrophilic side chains terminated with ion conducting sulfonic acid groups (\(\text{HSO}_3^-\))[4,8]. However, the Nafion membrane is expensive, vulnerable to crossovers of fuel and gas, and shows low proton selectivity [4,6,12]. Therefore, several new types of membrane have been reported using alternative proton (or ion) conductors [10,11]. Easy gas crossover through Nafion causes the inhibition of anode bacteria, exoelectrogens, by diffused oxygen from the cathode in the case of MFC. As for MEC, it also reduces hydrogen purity in the cathode compartment, by mixing with the gases produced in the anode compartment. Therefore, for commercial application of those technologies, it is important to develop alternative membranes to the expensive Nafion.

As a PEM material for a substitute of Nafion, sulfonated hydrocarbon-based polymers have been widely investigated to overcome the drawbacks of Nafion [10,11,13]. Among those hydrocarbon polymers, sulfonated polymer ether ketone (SPEEK) has been considered as a promising candidate material because of its unique features, showing lower cost, excellent mechanical properties, and easy preparation [7,9,14–17]. However, proton exchange capacity of SPEEK should be increased to obtain proton conductivity comparable to that of Nafion, which adversely causes high water uptake and swelling. Dimensional changes due to high swelling give rise to mechanical deterioration of the membrane, such as cracking and delamination from electrode in the cells. To solve these drawbacks of SPEEK, we suggest the concept of a composite membrane reinforced by a dimensionally stable substrate, without sacrificing ion conductivity. For reinforcement, polyimide nanofibers were embedded in the centre of SPEEK polymer matrix as three-dimensional supporting structures.

The authors developed an alternative SPEEK composite membrane to Nafion, which shows high proton selectivity, low crossovers of fuel and gas, and improved mechanical strength. It is a nanofiber-reinforced composite PEM (hereinafter referred to as NFR-PEM), impregnated with hydrocarbon polymer ion conductor, SPEEK.

This paper presents: (i) the mechanical properties of this novel PEM, (ii) its electrochemical features, such as micro-phase separation of hydrophobic and hydrophilic domains, through-plane resistance, transport number of proton and other competing cations, and (iii) fuel/gas crossovers, and its actual performance for MEC. All results were compared with those obtained by Nafion membrane as a control.

2. Materials and methods

2.1. NFR-PEM fabrication

The newly designed composite PEM consists of a proton-conducting hydrocarbon polymer, SPEEK, and polyimide nanofibers that are embedded in a polymer matrix (Fig. 1). The polyimide electrospun substrates with an average thickness of 27 ± 2 \(\mu\)m and porosity of 80% were provided by KOLON (South Korea), and the fiber thickness of the substrate was in the range of 500–1000 nm. The thickness of prepared composite PEM was approximately 40–68 \(\mu\)m. In this study, polyimide nanofiber was selected as a substrate for this composite membrane, because of its excellent thermal and dimensional stability. In addition, it is particularly appropriate for the preparation, because of its compatibility with a solution impregnating process, attributed to its high porosity and organic solvent stability. Polymer solution was prepared using SPEEK of 1.75 meq/mg ion exchange capacity obtained from Fumatech Inc. (Germany), and N,N-dimethylacetamide (DMAC) as a solvent. SPEEK impregnated composite membrane was prepared by adding the SPEEK/DMAC solution on the extended polyimide substrate over the glass plate, and subsequently dried at 80 °C for 6 h. Unreinforced membrane was also prepared as a control, by casting the same solution on a glass plate in a similar way, but without polyimide substrate. The membranes were acidified in a 1 N boiling sulfuric acid solution for 2 h, and washed with deionized water.

2.2. Water uptake and swelling ratio measurement

To evaluate the dimensional stability of the membrane, water uptake and swelling ratio were obtained by measuring the weight and dimensional (in thickness and area) difference between the hydrated and dried membranes. For comparison, unreinforced pure-SPEEK and Nafion membrane (50 ± 1 \(\mu\)m in thickness) were also measured. Water uptake, the difference in weight before and after hydration of membranes, is a fundamental measurement for PEM. For the evaluation of the water uptake and swelling ratio, membrane samples were dried at 80 °C under vacuum condition until a constant weight, and the dry weight (\(W_{\text{dry}}\)), area (\(A_{\text{dry}}\)) and thickness (\(T_{\text{dry}}\)) were measured. The dry membranes were then immersed in deionized water overnight at room temperature, and the weight and dimensions of wet membranes were immediately measured (\(W_{\text{wet}}, A_{\text{wet}}, T_{\text{wet}}\)), after removal of surface water by wiping off with absorbent paper. All experiments were conducted in quintuplicate to minimize experimental errors, unless otherwise stated. The water uptake (WU) and the swelling ratio in area (\(\Delta A\)) and thickness (\(\Delta T\)) were calculated, using the following equations.

\[
WU(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100
\]

\[
\Delta A(\%) = \frac{A_{\text{wet}} - A_{\text{dry}}}{A_{\text{dry}}} \times 100
\]

\[
\Delta T(\%) = \frac{T_{\text{wet}} - T_{\text{dry}}}{T_{\text{dry}}} \times 100
\]

2.3. Tensile strength measurement

To evaluate the mechanical properties of membranes under the operational environment of MEC, water-swollen membranes were prepared by dipping the membranes in deionized water for 2 h, and the tensile test was performed with a tension tester Instron 5967 (Instron Corp., USA) at room temperature. Samples of 50 mm gauge length and 20 mm width were tested at a crosshead speed of 50 mm/min (ASTM D882). At least 5 specimens of each membrane were tested and the values were averaged.

2.4. Membrane characterization

Membrane pretreatment, SEM analyses, and the crossovers for fuel and gas were conducted with the same apparatus described in previous study [4]. Electrochemical analyses, such as through-plane electrical resistance, transport number, and specific proton conductivity, were conducted according to a previous study [5]. Micro-phase separation of the membrane was analyzed with
atomic force microscopy (AFM) using a XE-100 (Advanced Scanning Probe Microscope, PSIA Inc., South Korea) with a non-contact measurement mode. A monolithic silicon-based cantilever with a tip radius of less than 8 nm (NANO WORLD Innovative Technologies, Switzerland) was used.

2.5. Gas and fuel crossover measurement

For gas crossover measurement, anode and cathode chambers of a MEC were flushed with nitrogen gas, and then a standard gas was filled into only the anode chamber. Both chambers contained 50% (v/v) deionized water, to prevent the membrane drying. The gas diffusion from anode to cathode through the membrane was then measured over time at a constant temperature of 25 ± 1 °C. For fuel crossover evaluation, 3 mM of acetate was initially fed only into the anode.

2.6. MEC performance test

Two-chambered MECs (180 mL working volume each) were constructed, and operated at a constant temperature of 25 ± 1 °C, according to the published procedure [18,19]. The MECs were equipped with a NFR-PEM, as well as a Nafion 117 membrane, as a control to compare their performance. The anolyte was a nutrient mineral buffer (pH 7.0) capable of supporting bacterial growth, while the catholyte was phosphate buffer solution (pH 7.0). The produced gas composition and concentration (H₂, CH₄, and CO₂) were analyzed using gas chromatography (GC-2010, Shimadzu, Japan) equipped with a thermal conductivity detector, and a molecular sieve column (CP-Polar PLOT A; 27.5 m × 0.53 m, 20 μm) with ultra-purified nitrogen (99.999%) as a carrier gas. To onset hydrogen production through MEC, a power supply (Agilent, USA) was utilized as the external power source, with an applied voltage of 500 mV. Acetate (1.3 mM) was used as the sole carbon source in all experiments.

3. Results and discussion

3.1. Morphology

Conventional hydrocarbon-based PEMs, such as SPEEK membranes, have an inevitable drawback of severe swelling due to hydration, as used in microbial fuel (or electrolysis) cells. The dry/wet cycles, probably happening during prolonged operation of MECs, lead to adverse dimensional changes that may increase mechanical deterioration, such as cracking and delamination. In the present study, this drawback was overcome by adopting membrane reinforcement with a nanofiber substrate. Fig. 1 shows SEM images of a cross-sectional view of the NFR-PEM, where polyimide nanofibers were embedded in a SPEEK polymer matrix. The thickness of nanofiber was approximately 500–1000 (average 700) nm, and its role is to minimize water swelling as hydrated, which led to an increase in dimensional and mechanical strength (as proved in Table 1 and Fig. 3). The NFR-PEM thickness was 40–68 μm, in which nanofibers were homogeneously distributed in the SPEEK matrix, without the introduction of any void space around the nanofibers that might be damaging for performance of the composite membrane. Some small pores shown around certain of the nanofibers were probably formed during the cryogenic fracturing for the SEM investigation.

3.2. Water uptake, dimensional change, and mechanical strength

Water uptake and swelling ratio are important parameters to determine proton conductivity, dimensional stability, mechanical properties, and fuel crossover through membranes. In general, the relationship of proton conductivity and water uptake is interdependent: high water uptake leads to high proton conductivity, because water molecules act as a transportation medium for protons in the hydrophilic domain of the membrane [7,20]. However, too high a water uptake leads to excessive swelling, especially in the planar direction, and poor mechanical stability, in particular with a delamination of the electrode in the membrane electrode assembly.
The results of electrochemical properties suggested that NFR-PEM exhibited higher proton conductivity compared to Nafion 117, indicating greater performance when they are used in the MECs. The NFR-PEM showed a through-plane resistance (=membrane electrical resistance (MER), at \( t = 20 \text{ min} \) of 1.24 ± 0.05 \( \Omega \text{ cm}^2 \) compared to 1.28 ± 0.07 \( \Omega \text{ cm}^2 \) for a Nafion 117 membrane, indicating the greater capability of transporting protons through the membrane (Fig. 4a). The proton transport number \( (t_p) \) of the NFR-PEM was 0.95 when measured with hydrochloric acid, which was higher than the 0.93 of Nafion 117 (Fig. 4b). In contrast, their sodium transport number (0.91) was less than that of Nafion 117 (0.93), indicating relatively higher proton selectivity of NFR-PEM. Cations are present in significantly higher concentration than protons in the anode chamber, due to their supply as a growth medium to optimize anodic bacterial growth condition [4–6]. These cations actively compete with protons for the negatively charged sulfonate groups in PEMs, because they also have a higher affinity for most other cation species [6]. As a consequence of losing the contact chance of protons being transported from the anode to the cathode chamber, protons are continuously accumulated in the anode compartment, which results in a serious pH decrease, and subsequent inhibitory influence on the anode bacteria. Therefore, the unique feature of the NFR-PEM, a higher affinity for protons, but less affinity for other cations, brightens its potential for MEC applications. In particular, the introduction of polyimide nanofibers, which are inactive for proton transport, does not sacrifice (as proven in Fig. 4) the performance of proton transport as a result of their higher porosity (80%).

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### 3.4. Gas and fuel crossover

Gas crossovers through PEMs are essential problems for MFC-based technologies. In conventional MFC using oxygen as an electron acceptor in the cathode, oxygen diffusion to the anode reduces Coulombic efficiency, due to its inhibitory effect on anode bacteria. In the case of MECs, in addition to a hydrogen loss through PEMs, an undesirable contamination of produced hydrogen gas with gases produced at the anode compartment, such as \( \text{CO}_2 \) and \( \text{CH}_4 \), is unavoidable, and alleviates the unique advantage of high hydrogen purity of the MEC over other methods for biological hydrogen production. Fig. 5 represents gas crossover through the membrane. As consistent with previous study [19], Nafion was quite permeable to gases. The NFR-PEM was twofold less permeable to all tested gases, including \( \text{O}_2 \), \( \text{CO}_2 \), \( \text{CH}_4 \), and \( \text{H}_2 \) compared to the Nafion: \( \text{CO}_2 \) and \( \text{H}_2 \) results were depicted in Fig. 5. Among tested gases, \( \text{CO}_2 \) was most rapidly diffused through PEMs, probably due to its high water solubility. In contrast to the gas permeability,
the NFR-PEM exhibited slightly lower acetate (substrate) permeability than a Nafion membrane (data were not shown).

The PEM polymer material presents a nanoscale structure made of cylindrical sulfonated ion cluster channels showing hydrophilicity; just enough to let water and protons and cations pass directly through them. According to the AFM analysis, the NFR-PEM showed better micro-phase separation without a significant aggregation of hydrophilic or hydrophobic domains, compared to a Nafion 117 (data were not shown). This more even distribution of hydrophilic and hydrophobic domains leads to reduction of sulfonated ion cluster channel size, while enhancing its tortuosity through a PEM. Therefore, this unique structural feature in our new PEM might decrease transport of cations with greater kinetic diameter than protons: the bigger cations are difficult to be transported through the ion passing channels, because they are too few, and are not being aligned straight through the membrane. Similarly, the relatively less gas crossovers of the new PEMs may be explained by the same aspect, compared with those of Nafion membrane. The results of this study are in agreement with the previous reporting that SPEEK membrane exhibits more resistance to fuel crossover than Nafion, due to its microstructural features, such as its narrower, more branched and more tortuous hydrophilic channels, with more dead-end pockets [11,15].

3.5. Hydrogen gas production performance of MEC

Fig. 6a shows the hydrogen gas production of MECs equipped with different PEMs. The installation of NFR-PEM into MECs represented much higher hydrogen production at the cathode, with an overall hydrogen efficiency ($e$ to hydrogen) of 86.4 ± 14.7%, as compared to 77.2 ± 10.3% of Nafion. The amount of hydrogen gas produced from NFR-PEM and Nafion was approximately 14.4 ± 2.4 mL and 12.9 ± 1.7 mL, respectively, at applied voltage of 500 mV. As expected, the trend of these results is in agreement with the gas crossover results shown in Fig. 5. The greater efficiency of NFR-PEM is attributed to less loss of both hydrogen gas and acetate through the membrane. Less loss of acetate led to an increase of available substrate for anode bacterial uptake. Nevertheless, the most important reason for the relatively higher performance is probably explained by a mitigated pH suffering to anode bacteria, since the NFR-PEM better facilitates the transports of the protons from anode to cathode without accumulation.

The pH imbalance caused by the accumulation of protons produced in the anode chamber is a serious problem in MFC-based technologies, especially in a fed-batch operation. As expected, based on electrochemical properties of NFR-PEM, the application of NFR-PEM significantly mitigates proton accumulation in the anode chamber when it was installed in MEC, as shown in Fig. 6b. This offers a preferential growth condition for anode bacteria, and consequently results in more enhanced production of hydrogen compared to Nafion. As three batch cycles of MEC were finished, pH values of the anode decreased from 6.93 ± 0.04 at the beginning to 6.78 ± 0.15 for NFR-PEM, and from 7.01 ± 0.06 to 6.26 ± 0.12 for Nafion 117, respectively, due to the accumulation of produced proton. Meanwhile, cathode pH values increased slightly from 7.02 ± 0.01 to 7.27 ± 0.03 for NFR-PEM compared to a severe increase from 7.02 ± 0.04 to 7.53 ± 0.03 for Nafion, due to the retardation of proton transport from anode to cathode.

To overcome this pH imbalance problem in MEC, single chambered membrane-less systems without a PEM have frequently been studied [21,22]. Those MECs are also attractive to increase performance, because they can reduce the internal ohmic resistance, by avoiding catholyte usage, as a result of combining two chambers. In the membrane-less systems, the elimination of membrane apparently facilitates proton transport, but offsets that merit by contaminating hydrogen gas with undesirable...
protons, and lower costs, by overcoming SPEEK’s weakness of the search for better membranes, because it possessed diverse and more resistant to fuel and gas crossovers. In these circumstances, materials that are as conductive as Nafion, but cheaper, stronger, and nanofibers as a supporter was developed. It showed practically viable. Is more conductive for protons, physically stable and economically viable. As an essential component, and thus this newly developed NFR-PEM can be an alternative membrane to Nafion, because it is more conductive for protons, physically stable and economically viable.

4. Conclusions

A new composite PEM consisting of SPEEK as a proton conductor, and nanofibers as a supporter was developed. It showed promising advantages over Nafion on performance, as used for MECs. The main task regarding PEMs is to develop substitute materials that are as conductive as Nafion, but cheaper, stronger, and more resistant to fuel and gas crossovers. In these circumstances, this newly developed PEM can give crucial insight in the search for better membranes, because it possessed diverse advantages over SPEEK membrane, such as a greater affinity to protons, and lower costs, by overcoming SPEEK’s weakness of mechanical instability.

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