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Characterization of uncharged and sulfonated porous poly(vinylidene fluoride) membranes and their performance in microbial fuel cells

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ABSTRACT

Uncharged porous PVDF and sulfonated porous PVDF membranes were prepared as alternative materials to Nafion membrane for application in a microbial fuel cell (MFC). Performances of Nafion, uncharged porous PVDF and sulfonated porous PVDF membranes in an air-cathode MFC were evaluated. Both uncharged and sulfonated porous PVDF membranes performed better than the Nafion membrane during MFC operation. The observed properties of low membrane electrical resistance, high ion exchange capacity, moderate oxygen permeability, and high ion selectivity also indicated that the sulfonated PVDF membrane is the most appropriate membrane for MFC applications. The uncharged porous PVDF membrane exhibited the lowest oxygen permeability resulting in a higher performance than the Nafion membrane. The impedance of the MFC systems was measured and analyzed with an equivalent circuit which accounts for the electrolyte (as media for microorganisms), both electrodes, and a membrane as components. It was found that the high performance of the sulfonated porous PVDF membrane is due to the low impedance of all components in the MFC. The sulfonated porous PVDF membrane, prepared for low resistance proton transport, is successfully applied to the MFC in this study.

1. Introduction

Microbial fuel cell (MFC) is a clean energy conversion system, which produces electricity directly from chemicals, especially organic compounds, by the aid of microbial activity. As the need for sustainable energy increases, the interest in the MFC also grows. The MFC consists of an anaerobic anodic compartment and an aerobic cathodic compartment, and protons are transported through a membrane separating these two compartments, as shown in Fig. 1. Instead of using a membrane, a salt bridge was applied at the very beginning of MFC development [1] and no separator was used in some cases. Many researchers have attempted to increase the efficiency by improving the individual MFC components. Researchers have also worked to discover the optimum conditions of MFC operation by applying various types of microorganism [2–4], media (fuel) [3–5], electrode materials/submaterials [6–10], and cell configurations [11–15]. The membrane is a highly influential component that affects the performance of the entire system because a large portion of the internal resistance of the MFC is owing to the membrane. Most researches that have focused on membranes may be categorized into two groups. The first group used a preselected membrane as a part of the system and evaluated the performance of the MFC by modifying the other parts of system. The latter group investigated the effect of the membrane on the MFC performance using various commercial membranes [11,16,17]. Only a few researchers have taken up the challenge of developing alternative membranes for MFC applications [5,18]. A commonly used membrane for MFCs is the commercially available Nafion membrane, which is frequently used for various fuel cell applications [19,20]. Although the Nafion membrane is still considered the best membrane for MFCs, its high cost of around $200 per m^2 and the high internal resistance of the resulting cells are the limiting factors for MFC applications [21]. The growing demand for MFCs necessitates further development of suitable membranes for specific MFC applications. With consideration for the conditions of system operation and cost reduction, a MFC membrane should have the characteristics of high proton conductivity, low internal resistance, oxygen impermeability, and low price relative to currently available membranes.

The high conductivity of porous membrane is already recognized [22,23], however, a few studies have applied porous membranes to MFC systems [11,24,25]. Kim et al. applied different types of commercial membranes to MFCs [11]. The results of Kim's study using a Nafion membrane and various porous membranes with different pore sizes suggest that porous membranes work adequately in MFCs and indicate the possibility of electricity production using porous membranes. The maximum power density generated using a porous membrane is similar to that of the Nafion

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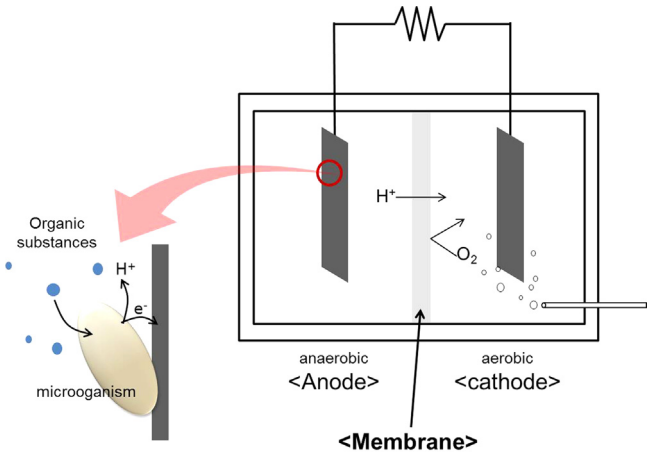

Fig. 1. A schematic diagram of a typical MFC configuration.

membrane. Zhang et al. employed several types of fiber filters as a separator for an air-cathode MFC [24]. Filters of various pore sizes were used and their performance in the MFC system was evaluated. It was shown that the performance of MFCs is highly affected by the internal resistance, which is increased by decreasing the pore size of the filters. In addition, the MFC performance with filters showed reasonable values relative to the MFC without a filter.

Even though the feasibility of applying porous membranes to the MFC system is substantiated by previous researches [11,24,25], a low-resistance functional membrane is still required for MFC application. Newly proposed membranes for MFCs should have higher performance and potentially lower production costs than commercial membranes. To achieve this goal, polyvinylidene difluoride (PVDF), which is a perfluorinated polymer and known for its high chemical, thermal, and mechanical resistance, was used. In addition, PVDF is less expensive than Nafion, and, consequently, the production cost of the membrane is lower than that of the Nafion membrane. In this study, an uncharged porous PVDF membrane was first prepared as a base membrane. Subsequently, a porous proton exchange membrane was prepared by functionalization of the base membrane. The ionic functional group acts as an ion exchanger in the membrane and extensively affects the transport and selection of ions passing through the membrane. For example, the sulfonic acid group is commonly used as a functional group for cation exchange membranes, which allows cations to selectively permeate through a membrane. Therefore, in this study, sulfonation of uncharged porous PVDF membranes was carried out and tested for an air-cathode MFC system to enhance the cationic transport and lower the resistance of the uncharged PVDF membrane.

2. Experimental

2.1. Materials

Nafion membrane (NAF NR212) was obtained from DuPont Co. (Wilmington, DE, USA). Poly(vinylidene fluoride) (PVDF, M_W= 275,000, ρ=1.78 g/cm^3), *N*,*N*-Dimethylformamide (DMF, 99.8%), 1-butanol (BuOH, 99.8%), mineral oil (ρ=0.838 g/cm^3), D(+)-glucose, sodium phosphate monobasic (NaH_2PO_4), sodium phosphate dibasic (Na_2HPO_4), Nafion 117 solution (5%), 2-propanol (99.5%), nitric acid (70%), methanol (99.8%), styrene, tetrahydrofuran (THF, 99.9%), benzoyl peroxide (BPO, 75%), chloroform (99%), and 1,2-dichloroethane (DCE, 99.8%) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Sodium chloride (99.5%), sulfuric acid (95%), and potassium hydroxide (99.0%) were supplied by OCI Company Ltd. (Atlanta, GA, USA). Hydrochloric acid (1 M standard solution) and sodium hydroxide (0.1 and 0.01 M standard solutions) were obtained from Samchun Pure Chemical (Gyeonggi-do, Republic of Korea). Phenolphthalein solution (0.1%) was purchased from Daejung (Republic of Korea). Yeast extract was provided from Fluka (Sigma-Aldrich, St. Louis, MO, USA). The gas diffusion layer (GDL 35BC) was obtained from SGL group – The Carbon Company (Wiesbaden, Germany). Graphite felt (GF-20-5F) was supplied by Nippon Carbon Co. Ltd. (Tokyo, Japan). Pt–C powder (37% Pt) was purchased from Tanaka Kikinzoku Kogyo K.K. (Tokyo, Japan).

2.2. Membrane preparation

The Nafion membrane was pre-treated by immersion in 1 M HCl solution for more than 5 h and rinsed with DI water [26]. The uncharged porous PVDF membrane (which is henceforth called the “uncharged PVDF membrane”) was prepared by the wet-phase inversion method. The PVDF was dissolved in DMF with a concentration of 15 wt% and then 20 wt% of 1-butanol was added as a non-solvent additive. The solution was cast on a glass plate using a doctor blade to produce a film having a thickness of around 200 μm and the cast film was immediately immersed in DI water. All prepared membranes were soaked in DI water for at least 24 h before use. The porous cation exchange membrane (hereinafter the “sulfonated PVDF membrane”) was prepared by a grafting polymer reaction followed by sulfonation using the uncharged PVDF base membrane as shown in Fig. 2. The styrene grafted porous PVDF membrane was prepared as follows [27]. (1) The membrane was first soaked in 0.05 M potassium hydroxide dissolved in methanol at 80 °C for 45 min. (2) After washing the membrane with DI water, the membrane was immersed in a styrene and THF mixture in the ratio of 8:1 with a 2 g/L BPO concentration at 80 °C for 16 h. (3) The membrane was then washed with chloroform. The styrene grafted PVDF membrane was immersed in DCE at 60 °C for 2 h and then the membrane was

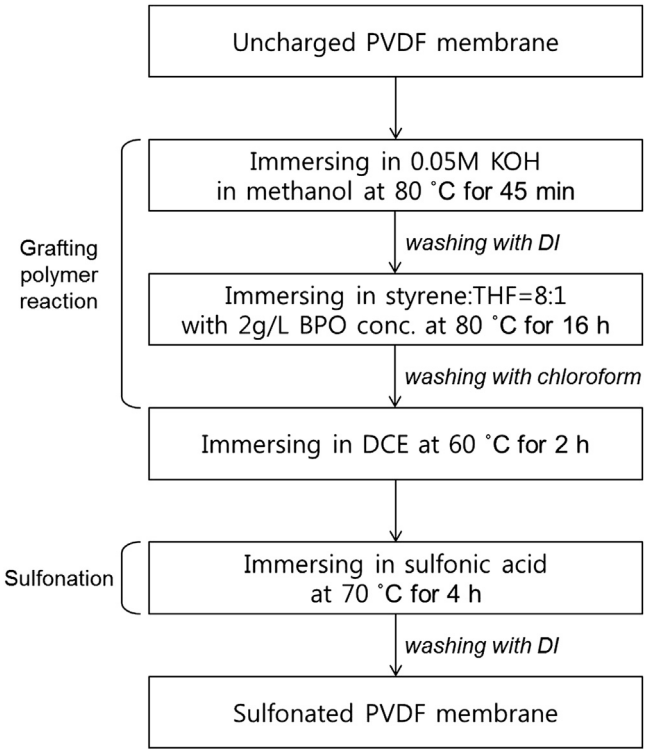

Fig. 2. A synthetic scheme of the sulfonated PVDF membrane.