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# Poly(arylene ether ketone) with pendant pyridinium groups for alkaline fuel cell membranes

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## ABSTRACT

Using the step-growth polycondensation reaction, poly(arylene ether ketone) (PAEK) and activated poly(arylene ether ketone)-NHS intermediates (PAEK-N) were synthesized. PAEK-NHS intermediates with pyridinium groups (PAEK-PYR) were obtained by adding different amounts of PYR groups. The successful syntheses of PAEK, PAEK-N, and PAEK-PYR were confirmed by nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy. Several important membrane properties (e.g., ionic exchange capacity (IEC), water uptake, anion conductivity, and thermal and mechanical stability) were investigated for their applications in alkaline fuel cells. Water uptake, swelling ratio, anion conductivity, and IEC increased with increasing PYR contents, while the mechanical properties decreased. Among a series of prepared membranes, the PAEK-PYR100 and PAEK-PYR125 membranes showed IEC and anion conductivity values that were higher than those of a commercial AHA membrane. Also, all of the prepared membranes were thermally stable up to 255 °C and show excellent chemical stability in alkaline conditions.

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## Introduction

It is of global importance that the greenhouse gas emissions associated with energy production be substantially reduced [1]. As the level of fossil fuel consumption has increased rapidly due to the development of industry and human life, the growing demand for alternative energy sources has become a critical issue. Among various solutions to such energy-related problems, fuel cells are promising because they enable the direct conversion of chemical energy into electrical energy using environmentally-abundant and -friendly reaction sources such as hydrogen and oxygen. Among the variety of types of fuel cells, two types are categorized as “low-temperature fuel cells” because their operating temperatures are not more than 120 °C: alkaline fuel

cells (AFCs) and proton-exchange membrane fuel cells (PEMFCs) [2,3].

In PEMFCs, proton exchange membranes are used as solid electrolytes to transport protons from the anode to the cathode [4]. Presently, commercial proton exchange polymer membranes, represented by Nafion<sup>®</sup>, are based on per-fluorosulfonic acid and exhibit excellent mechanical, chemical, and thermal stability as well as high proton conductivity. Nafion<sup>®</sup> membranes, however, are costly and not eco-friendly due to the waste created and regeneration of fluorinated polymers. Moreover, the high cost of platinum catalysts, harmful waste emissions (carbon monoxide gas) at low temperature, and short lifetimes of PEMs are critical barriers for commercialization of PEMFCs. For these reasons, alkaline exchange membrane fuel cells (AEMFCs) are believed to represent a superior alternative to PEMFCs [5,6].

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In AFCs (including AEMFCs), the oxygen in air is reduced at the cathode to produce hydroxide ions. These ions are transferred through the electrolyte to the anode, where the hydrogen is oxidized by hydroxide ions to form water. A traditional AFC uses a potassium hydroxide (KOH) aqueous solution as an electrolyte because of its high conductivity. However, a major problem in this traditional AFC is the deactivation of the electrolyte and electrodes caused by the formation of carbonate/bicarbonate ( $\text{CO}_3^{2-}/\text{HCO}_3^-$ ) via the reaction of KOH ions with contaminants in the oxidant gas stream (e.g.,  $\text{CO}_2$ ) [7]. The production of carbonates considerably lessens the hydroxide ion conductivity of the electrolyte and the reaction rate of the electrolyte.

A solid electrolyte system has been proposed as a replacement for this liquid electrolyte. AEMFCs are fuel cells that use a solid anion-exchange polymer membrane as the electrolyte. Compared with PEMFCs, AEMFCs show superior inherent oxygen reduction kinetics and fuel oxidation kinetics, which enable the use of less expensive metal catalysts (such as nickel and silver) [8–12]. To obtain efficient AEMs, the membranes must achieve both high ionic conductivity and strong mechanical stability. The ionic conductivity can be improved by increasing the amount of anion conductive groups (functional groups) in the membrane; however, this treatment is generally accompanied by a reduction in the mechanical properties due to the fact that large amounts of water are absorbed in the membrane. Therefore, a new type of structure should be developed to enhance the mechanical properties of the AEM. Additionally, another important factor that should be considered is the price. The cost of a typical commercial AEM (the Neosepta AHA membrane; Tokuyama Co. Ltd. in Japan) is currently comparably as expensive as Nafion®.

The introduction of OH-transferrable functional groups into the polymer backbone is very important for the preparation of AEMs. Quaternary ammonium (QA) has been the most extensively studied functional group for the preparation of AEMs. The most important problem related to QA is that it causes degradation of the membrane by Hoffmann elimination and  $\text{S}_{\text{N}}2$  displacement under high pH and temperature [13–15]. Also, the introduction of QA groups into the polymer backbone is typically performed by a chloromethylation reaction. However, because this reaction is very difficult to control (due to its easy gelation) and very harmful to the human body, it has been used sparingly.

For these reasons, many efforts have been made to develop AEMs without QA groups. In this study, we propose a functional group (i.e., pyridinium) that is quite different from conventional QAs, where the big  $\pi$ -bond-conjugated system yields pyridinium salts with superior thermal and chemical stabilities [16]. Also, the pyridinium groups are not positioned at the backbone site but are instead located at the pendant site to avoid the chloromethylation reaction and to improve ionic aggregation (phase separation); this leads to higher conductivity and improved mechanical strength in the resultant material. Poly(arylene ether ketone) (PAEK) was used as a backbone material because it has excellent thermal, mechanical, chemical, and dimensional stability [17–23]. In this study, poly(arylene ether ketone) with carboxylic acid was

first synthesized via a direct step-growth polycondensation reaction. Poly(arylene ether ketone), with pendant pyridinium groups, was then synthesized by an amidation reaction from the activated carboxylic acid groups of PAEK and the amine groups of 4-picolyanamine. The IEC, anion conductivity, water uptake, swelling ratio, chemical stability, and mechanical properties were investigated.

## Experimental

### Materials

4, 4-Bis(4-hydroxyphenyl)-valeric acid, iodomethane, potassium carbonate ( $\text{K}_2\text{CO}_3$ ), N-hydroxysuccinimide (NHS), and N,N'-dicyclohexylcarbodiimide (DCC) were purchased from Sigma–Aldrich (USA). 4,4-Difluorobenzophenone, N,N'-dimethylacetamide (DMAc), N,N'-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), and 4-picolyamine (PYR) were purchased from Tokyo Chemical Industry (TCI, Japan). Toluene, isopropanol, and methanol were obtained from Samchun Chemical (Korea), and hydrochloric acid and sodium hydroxide beads were purchased from Duksan Chemical (Korea) and Daejung Chemical (Korea), respectively.

### Synthesis of poly(arylene ether ketone) (PAEK), activated PAEK-NHS intermediates (PAEK-N), and PAEK-NHS intermediates with pyridinium groups (PAEK-PYR)

PAEK was synthesized via a step-growth condensation reaction. 4,4-Bis(4-hydroxyphenyl)-valeric acid (0.01 mol), potassium carbonate ( $\text{K}_2\text{CO}_3$ ) (0.025 mol), DMSO (45 mL), and toluene (40 mL) were placed in a three-neck round-bottom flask with a stirrer. The mixture was continuously stirred for 12 h under a nitrogen atmosphere at room temperature (RT). The mixture was heated up to 145 °C for 5 h and then cooled to RT. 4,4-Difluorobenzophenone (0.01 mol) and DMSO (10 mL) were added to the reactor. After stirring for 12 h, the mixture was heated to 145 °C for 6 h, and then the temperature was increased to 170 °C, where the polycondensation reaction was carried out for 24 h. When the mixture was cooled to RT a solid white precipitate was obtained. The solid was dissolved in a mixture of 27 mL of THF and 8 mL of HCl. Next, the polymer solution was added to 600 mL of isopropanol (IPA). The PAEK product was washed several times with deionized water (DI) and IPA and then dried at 60 °C under vacuum for 24 h.

By converting all of the carboxylic acid groups of PAEK to NHS esters, PAEK-N was synthesized. PAEK (0.005 mol), NHS (0.006 mol), and DCC (0.006 mol) were dissolved in DMF. The solution was stirred at RT for 12 h and then heated to 40 °C for 18 h. After cooling to RT, the mixture was filtered to remove the impurities and suspended solid. The solution was dropped into 600 mL of IPA under stirring to obtain the precipitate product. The precipitate was washed with IPA and methanol several times and then dried under vacuum for 24 h at 40 °C to obtain the white PAEK-N solid powder.

PAEK-N (0.001 mol) was dissolved in 10 mL of DMAc solvent and stirred with a magnetic bar for 30 min to completely

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