



Anion-exchange membranes based on poly(arylene ether ketone) with pendant quaternary ammonium groups for alkaline fuel cell application



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ABSTRACT

Poly(arylene ether ketone)s (PAEKs) with pendant quaternary ammonium groups were synthesized via a direct step-growth polycondensation reaction to prepare anion exchange membranes (AEMs) for alkaline fuel cells. The chemical structure of the synthesized quaternary ammonium PAEK was confirmed by ^1H nuclear magnetic resonance spectroscopy (^1H NMR), Fourier transform infrared (FT-IR) spectroscopy and energy dispersive X-ray (EDX) spectroscopy. Three types of PAEK based membrane with different alkyl chain lengths in the amine core were synthesized and their properties were compared. The anion conductivity of the prepared PAEK membranes decreased with aminated alkyl length. The membranes aminated with the trimethylamine (PAEK-TMA), triethylamine (PAEK-TEA), tripropylamine (PAEK-TPA) 0.014, 0.003, and 0.0008 Scm^{-1} at 40 °C and 0.021, 0.006, and 0.0014 Scm^{-1} at 80 °C, respectively. While the PAEK-TMA, PAEK-TEA, and PAEK-TPA membranes exhibited different ionic conductivities, they showed quite low water uptake – 15.8% at 30 °C and 26.9% at 90 °C for PAEK-TMA, 11% at 30 °C and 17.6% at 90 °C for PAEK-TEA, 10.7% at 30 °C and 16.5% at 90 °C for PAEK-TPA. Such high anion conductivity and low water uptake of the prepared membranes are potential advantages for their application in AEMs.

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1. Introduction

Natural fuels such as wood, coal, natural gas, and petroleum products continue to be our main energy sources for converting heat energy into electrical energy, despite being non-renewable. Furthermore, their consumption leads to increasing environmental pollution. Utilization of other natural energy resources such as water flow, wind, sunlight, and especially nuclear energy requires much higher technology with higher risk.

Fuel cells are a good substitute for natural fuel sources. A fuel cell is an electrochemical device that uses chemical energy sources (hydrogen, methanol...) and converts them into electrical power directly [1]. Basically fuel cells can be divided into several types: proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cell (DMFC), alkaline fuel cells (AFCs), solid oxide fuel cells (SOFCs), molten carbonate fuel cells (MCFCs), and phosphoric acid fuel cells (PAFCs) [2]. Among those, polymer membranes are frequently used as electrolytes in PEMFC and DMFC. Polymer electrolyte membranes and catalysts are the main components in the fabrication of membrane electrode assembly (MEA). Many studies

have been conducted to reduce its cost and enhance its performance. Although the performance of MEA was significantly enhanced by the development of new membranes, its cost has not been greatly reduced due to the high cost of the platinum catalyst.

Compared to PEMFC, the main advantage of AFC is that it can use ordinary metal catalysts for the electrode, such as iron, nickel, and silver. As AFC requires the anion exchange function in electrolyte membranes, it offers the further twin advantages over PEMFC of having lower activation loss in alkaline medium and lower oxidant-reduction over-potential at high pH in order to increase the efficiency [3,4].

Originally, liquid electrolyte-based alkaline fuel cells were used for space applications. However, the carbonate salts contained in liquid electrolytes occasionally block the pores of the catalyst electrode and limit the fuel cell's efficiency. Currently, the development of solid polymer membranes to replace the liquid electrolyte has resulted in reports of many polymers such as ion-solvating polymers (PEO/KOH [5–8]), PBI/KOH [9], alkoxy silane [10], PPO-Si(OCH₃)₃(+) [11], PPO-Si(OCH₃)₃(+), Eph/TEOS [12,13], PMA-SiO₂ [14], PVA/TiO₂ cross-linked polymers [15]).

Among various solid polymer materials that have been applied in AFC membranes, poly(arylene ether ketone) (PAEK) has great potential because of its excellent thermal and mechanical properties, and chemical resistance [16–23]. While extensive results

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have been reported on its application in PEMFC and DMFC, including our previous works [28,29], few studies have examined its application in AFC. It was reported that PAEK with pendant ammonium groups was not stable when synthesized at high temperature [24–26]. Also, as PAEK containing a phosphonium or guanidinium head-group requires expensive agents such as tris (2,4,6-trimethoxyphenyl)phosphine and pentamethylguanidine, alkylamines such as trimethylamine (TMA), triethylamine (TEA), and tripropylamine (TPA) are alternatives for quaternarization in order to decrease the cost while maintaining high performance [4,27]. In the synthesis and characterization of hydroxyl exchange membranes, few works have reported on the use of pendant quaternary ammonium groups on the side chain [33–36].

In this work, we synthesized a new type of PAEK-based electrolyte containing pendant quaternary ammonium groups for application in anion exchange membranes (AEMs). PAEK was directly polymerized from monomers, 4,4-difluorobenzophenone and valeric acid containing carboxyl group on side chain. The resulting polymers were quaternarized by TMA, TEA, or TPA, then alkalinized by NaOH solution to compare the ionic conductivity among TMA, TEA, and TPA-quaternarized membranes.

2. Experimental

2.1. Materials

4,4-Bis(4-hydroxyphenyl)-valeric acid, potassium carbonate (K_2CO_3), N,N'-dicyclohexylcarbodiimide (DCC), N-hydroxysuccinimide (NHS), and 2-bromoethylamine (BEA) were purchased from Aldrich Chemical Company (Aldrich, Milwaukee, WI, USA). 4,4'-Difluorobenzophenone, dimethylsulfoxide (DMSO), N, N-dimethylacetamide (DMAc), tetrahydrofuran (THF), TMA, TEA, and TPA were purchased from Tokyo Chemical Industry (TCI, Japan). Toluene, isopropanol, and methanol were obtained from Samchun Chemical Company (Samchun, Korea). Hydrochloric acid (HCl) was purchased from Duksan Chemical Company (Duksan, Korea).

2.2. Synthesis of PAEK-COOH and PAEK-NHS precursors

PAEK with pendant carboxylic acid (PAEK-COOH) was synthesized via a direct step-growth polycondensation reaction from two monomers, 4,4-bis(4-hydroxyphenyl)-valeric acid and 4,4'-difluorobenzophenone [28]. Dry DMSO (45 g), toluene (40 g), 4,4-bis(4-hydroxyphenyl)-valeric acid (0.01 mol), and K_2CO_3 (0.025 mol) were added to a 250 mL three-necked round bottom flask equipped with a Dean-Stack trap, a stirrer and a nitrogen gas inlet. The mixture was continuously stirred for 8–12 h at room temperature. The temperature was then raised to 145 °C and the mixture was refluxed for 4 h. Subsequently, the reaction mixture was cooled to room temperature and continuously stirred for 12 h after adding 4,4'-difluorobenzophenone (0.01 mol). The temperature was raised again to 145 °C for 4 h and then to 165 °C for 24 h until the polymeric precipitate was produced. The mixture was cooled to room temperature and the precipitate was dissolved in a mixture of 20 mL of THF and 7 mL of HCl aqueous solution (35%). The polymer solution was then dropped in isopropanol for recrystallization and the precipitate was washed with isopropanol three times. The solid product was washed three times with deionized (DI) water before drying at 60 °C for 24 h under vacuum. The synthetic scheme of PAEK-COOH is shown in Fig. 1.

1H NMR (DMSO- d_6 , ppm) 1, 1.59; 2, 1.90; 3, 2.49; 4, 12.04; 5, 7.05; 6, 7.26; 7, 7.75.

All of the pendant carboxylic acid groups in PAEK-COOH were replaced by NHS groups. For the preparation of PAEK with pendant

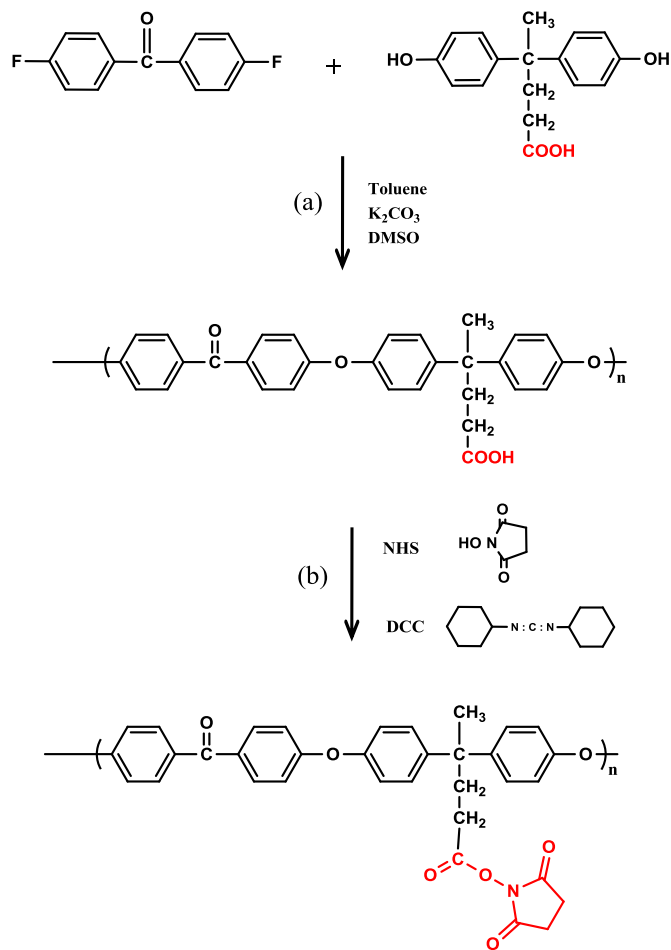


Fig. 1. Synthetic pathway of (a) PAEK-COOH and (b) PAEK-NHS precursors.

NHS groups (PAEK-NHS), PAEK, NHS and DCC were mixed in the mole ratio of 5:6:6 in dry DMF solvent. The mixture was stirred at room temperature for 12 h and then heated to 40 °C for 12 h under continuous stirring. After cooling, the reaction mixture was filtered to separate the suspended solid and the polymeric solution. The polymeric solution was continuously precipitated by dropping slowly into isopropanol under stirring with a magnetic bar. The polymeric solid was then washed a few times with isopropanol and methanol. The final product, PAEK-NHS, was obtained after drying at 40 °C under vacuum for 24 h. The synthetic scheme of the PAEK-NHS is shown in Fig. 1 [29].

1HNMR (DMSO- d_6 , ppm) 1, 1.59; 2, 1.90; 3, 2.49; 4, 2.77; 5, 7.05; 6, 7.26; 7, 7.75.

2.3. Preparation of PAEK membranes

First, 0.4 g of PAEK-NHS was dissolved in 5 mL DMAc and stirred with a magnetic stirring bar for 5 h. Next, BEA was added to the solution and stirred for 3 h continuously to prepare BEA-terminated PAEK (PAEK-BEA). The same mixtures were cast on glass petri dishes and dried at 60 °C for 12 h in atmosphere, and then at 85 °C for 24 h under vacuum. The membranes were peeled off from the petri dish and immersed firstly into TMA, TEA and TPA separately for quaternarization for 24 h at 40 °C and secondly in 1 M NaOH aqueous solution for alkalinization for 24 h at the same temperature. The aminated membranes were then washed with DI water a few times and immersed in water for storage. The resulting membranes were homogeneous and transparent with a thickness of 250–280 μm . Fig. 2 shows the synthesis procedure of

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