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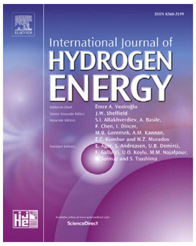

Chemically modified poly(arylene ether ketone)s with pendant imidazolium groups: Anion exchange membranes for alkaline fuel cells

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ABSTRACT

Anion exchange membranes (AEMs) with high stability are prepared for alkaline fuel cells using poly(arylene ether ketone)s (PAEKs) containing pendant imidazolium groups (via a direct step-growth polycondensation reaction). ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR) and Fourier transform infrared (FT-IR) spectroscopy are used to analyze the chemical structure of the prepared PAEK membranes. The anion conductivity, water uptake and swelling ratio, thermal, mechanical, and chemical stability of these membranes are investigated for PAEK membranes with different 1-(3-aminopropyl)imidazole (API) molar ratios (PAEK-API-x) in details. The anion conductivity of PAEK-API-x membranes increases with increasing molar ratio of API. The membrane with API 1.5 equiv. displays the highest anion conductivity (0.0053–0.0531 S cm^{-1} from 30 °C to 80 °C). All prepared membranes show good chemical and mechanical stability as well as thermal stability up to 250 °C. This high anion conductivity with good thermal, mechanical, and chemical stability of the membrane show potential advantage to meet the demands for AEMs.

Introduction

As fuel cell is a safe and green energy conversion device for stationary and mobile applications, it becomes a solution for producing clean and efficient energy for the next generation. Generally, fuel cells work based on transferring ions through the electrolyte membrane between the anode and cathode. The high ionic conductivity and mechanical stability of membrane make a fuel cell a promising energy source. Improved performance and enhancing durability of electrolyte membranes are currently areas of intense research and remain significant challenges. The ion transporting mechanism of the electrolyte forms many types of fuel cells such as proton exchange membrane fuel cells [1–4], alkaline fuel cells [5,6], solid oxide fuel cells [7], molten carbonate fuel cells [8], and phosphoric acid fuel cells [9]. Among them, the alkaline fuel cell is known as the most developed technology. As the liquid electrolyte-based alkaline fuel cells were operated in devices with disadvantages (limited performance and operating lifetime) [10] in the beginning, they were gradually replaced by alkaline anion exchange membrane fuel cells. There are, however, still many advantages to an alkaline anion exchange membrane in a fuel cell: 1) inexpensive non-noble metal catalysts (nickel, manganese oxide, silver, and iron) are used due to the low over-potentials associated with electrochemical reactions at high pH [11], 2) undesirable fuel crossover is reduced because the direction of alkaline anion

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(OH^-) transport opposes the direction of the fuel flux through the membrane [12], 3) the fuel oxidation and oxygen reduction reactions exhibit inherently faster kinetics in the high pH environment [13]. Therefore, there is increasing interest in the development of alkaline anion exchange membrane fuel cell as a promising technology for producing clean energy.

Literature survey shows that quaternary ammonium group based alkaline anion exchange electrolyte membrane exhibits improved performance for fuel cells [14–19]. However, the utilization of volatile hazardous reagents such as trimethylamine and triethylamine, etc. for introducing quaternary ammonium groups in the membrane is unfriendly to the environment [20]. Additionally, quaternary ammonium groups showed low thermochemical stability in a high pH medium due to the strong nucleophilicity of the OH^- anions [21,22]. Then guanidinium and phosphonium head groups were employed to enhance the stability of the anion exchange membrane [23,24], but they were ineffective due to high cost. The imidazolium head group is considered as a solution to the problem and reduces the price, while still maintaining the high performance of the anion exchange membrane. Compared to the quaternary ammonium group, the imidazolium group possesses π-conjugated structure of the five-member heterocyclic ring, which results in significantly low degradation of the imidazolium group in high pH medium. Because a conjugated structure of imidazolium ring causes the resonance effect which delocalizes electrons and lower the overall energy of the ring, the hydroxide ions weakly attack on imidazolium cations and thus the stability of imidazolium groups increases. In addition, the imidazolium head group based membrane exhibited higher ionic conductivity and thermal stability [25,26]. To date, many works have been reported due to interesting property of the imidazolium group for alkaline anion membranes [27–30].

In this study, we chemically modified the poly(arylene ether ketone)s with pendant imidazolium groups to make a promising electrolyte in an alkaline anion exchange membrane. PAEK is a great solid polymer material for anion exchange membranes due to excellent thermal, mechanical and chemical resistance properties [31–38]. In this synthetic scheme, the strong point is the synthetic method for functionalization of imidazolium in PAEK structure. Modified PAEK was directly synthesized via a step-growth polycondensation reaction from 4,4-diflourobenzophenol and valeric acid containing carboxyl group on the side chain. Carboxyl (–COOH) pendant groups of PAEK were easily modified to attach imidazolium groups through NHS intermediate reaction step. This route avoided the toxic reaction of chloromethylation. Moreover, long pendant chains with imidazolium head groups of PAEK increase the mobility of imidazolium cations, which is a very important factor to feasibly create ion clusters for anion-conducting channel formation. Further functionalization produced the PAEKs with various ratios of pendant imidazolium groups and was quaternarized by CH_3I and alkalizated by a KOH solution for alkaline anion exchange membrane performance. A series of PAEK-API-x membranes with as such pendant imidazolium groups are expected to show high anion conductivity and chemical and mechanical stability for alkaline fuel cell application.

Experimental

Materials

Methyl iodide (CH_3I), 4,4-bis(4-hydroxyphenyl)-valeric acid, *N*-hydroxysuccinimide (NHS), *N*,*N*′-dicyclohexylcarbodiimide (DCC) and potassium carbonate (K_2CO_3) were purchased from Aldrich, USA. 1-(3-Aminopropyl)imidazole (API), 4,4′-difluorobenzophenone, tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and *N*,*N*-dimethylacetamide (DMAc) were purchased from Tokyo Chemical Industry (TCI, Japan). Methanol, isopropanol, and toluene were purchased from the Samchun (Samchun, Korea), and hydrochloric acid (HCl) was purchased from Duksan (Duksan, Korea). The commercial AHA membrane was purchased from Tokuyama (Tokuyama Co., Japan).

Synthesis of PAEK-COOH and PAEK-NHS precursors

The poly(arylene ether ketone) with pendant carboxylic acid (PAEK-COOH) was synthesized by direct step-growth polycondensation reaction [19]. Here, 4,4-bis(4-hydroxyphenyl)-valeric acid and 4,4′-difluorobenzophenone were used as monomers in the reaction. In the typical synthesis, 0.01 mol of 4,4-bis(4-hydroxyphenyl)-valeric acid and 0.025 mol of K_2CO_3 was dissolve in a mixture of DMSO (45 g) and toluene (40 g) in a 250 mL flask with a stirrer, nitrogen gas inlet, and Dean-Stack trap. In this step, the mixture was stirred for 12 h at 25 °C. The temperature of mixture gradually increased up to 145 °C and refluxed for 4 h to remove the absorbed water. After that, the reaction mixture was cooled to ambient temperature and 0.01 mol of 4,4′-difluorobenzophenone was added into the flask. The resultant mixture was stirred for 12 h. When the mixture became homogeneous, the temperature of the mixture was gradually increased and set to 145 °C for 1 h, 150 °C for 12 h, and 168 °C for 24 h. After completing the reaction, the produced polymeric precipitate was separated from the solvent. 7 mL of HCl aqueous solution (35%) and 20 mL of THF mixture was added to dissolve the precipitate. The solution was filtered to remove salt by-product and then filtrate was added in isopropanol solvent for recrystallization. The polymer precipitate was separated and washed several times with isopropanol and deionized (DI) water. The polymer was dried under vacuum at 60 °C for 24 h. The details pathway of the PAEK-COOH synthetic scheme is shown in Fig. 1.

Further the functionalization of PAEK-COOH with pendant NHS groups was carried out. PAEK-COOH, *N*-hydroxysuccinimide (NHS) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) were mixed in dry DMF solvent with molar ratio 5:6:6. At 25 °C the mixture was stirred for 12 h. The temperature of the mixture was increased to 40 °C and stirred 12 h. After completing the reaction, the suspended solid was removed by filtration. The clean PAEK-NHS solution was added into isopropanol under continuous stirring for precipitation of polymer. The PAEK-NHS solid precipitate was washed with isopropanol and methanol several times. Pure PAEK-NHS was obtained after drying under a vacuum at 40 °C for 24 h. The pathway of the synthetic scheme of the PAEK-NHS is also shown in Fig. 1.

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