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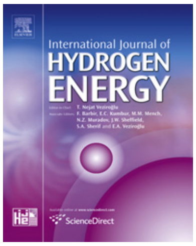

Anion conductive poly(tetraphenyl phthalazine ether sulfone) containing tetra quaternary ammonium hydroxide for alkaline fuel cell application

Dong Wan Seo, Young Don Lim, Mohammad Awlad Hossain, Soon Ho Lee, Hyun Chul Lee, Ho Hyoun Jang, Seong Young Choi, Whan Gi Kim[*]

Department of Applied Chemistry, Konkuk University, Chungju, Chungbuk 380-701, Republic of Korea

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ABSTRACT

The poly(tetraphenyl ether ketone sulfone)s (PTPEKSs) were synthesized from 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenyl benzene (BFBTPB) and bis(4-fluorophenyl) sulfone with bis(4-hydroxydiphenyl) sulfone in sulfolane. The synthesis of poly(tetraphenyl phthalazine ether sulfone)s (PTPPESs) was carried out via an intramolecular ring-closure reaction of dibenzoylbenzene moiety with hydrazine monohydrate. The PTPPES-QAHs [poly(tetraphenyl phthalazine ether sulfone-quaternary ammonium hydroxide)]s were synthesized via chloromethylation of PTPPES, quaternization with trimethylamine, and followed by an anion exchange of tetra-quaternary ammonium chloride polymers with KOH. Different contents of quaternized unit in PTPPES-QAH (15, 20, 25 mol% of BFBTPB) were studied by FT-IR, ^{1}H NMR spectroscopy, and thermogravimetric analysis (TGA). Sorption experiments were conducted to observe the interaction of quaternized polymers with water. The ion exchange capacity (IEC), ion conductivity and cell performance of PTPPES-QAH were evaluated with increasing the degree of quaternization.

1. Introduction

The proton exchange membranes commonly used in the proton exchange membrane fuel cells (PEMFCs) are the sulfonated fluorocarbon polymer like Nafion membranes (DuPont, USA). They show excellent chemical, mechanical and thermal stability and high ionic conductivity. However, they suffer from such disadvantages as limited operation temperature (0–80 °C), high cost, high methanol permeability and environmental incompatibility. The dependence of platinum catalysts is in essence a problem of limited natural resource rather than a matter of price only. Recently, a new concept of fuel cell using anion exchange membrane with more options for the cathode catalysts from nonprecious metals (such as nickel and silver) has been proposed [1–5]. Such fuel cell, namely anion exchange membrane fuel cell (AEMFC), can potentially reduce the above mentioned drawbacks of PEMFC [6]. These alkaline fuel cells have numerous advantages over proton exchange membrane fuel cells on both cathode kinetics and ohmic polarization. Anion exchange membrane fuel cell (AEMFC) is designed to provide sufficient hydroxyl ions for ion exchange during electrochemical reactions in alkaline fuel cells. It is important to study a wide range of routes to highly conductive, robust anion polymer exchange membranes and to develop the key structure–property relationships for these types of ion-

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[*] *Corresponding author*. Tel.: +82 43 840 3579; fax: +82 43 851 4169.
E-mail address: wgkim@kku.ac.kr (W.G. Kim).

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conducting membranes. However, a critical challenge for conventional AFCs is the use of aqueous alkaline electrolytes, which can react with CO_2 from air to form carbonate salts by the following reaction(s): $CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$ and/or $CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$. As a result, the performance of the fuel cell would quickly deteriorate. To solve this problem, recent investigations focused on intrinsically OH^- conducting alkaline polymer electrolyte (APE) materials to replace the alkaline electrolytes. By using APEs, the formation of carbonate salts can be prevented, which is attributable to the absence of metal ions. However, carbonate ions might still be formed through a reaction with CO_2, which would result in a reduced OH^- conductivity [7–9]. Application of APEs can also enable a compact design [10] and eliminate corrosion from alkaline solutions. There have been significant advances in the synthesis of quaternary ammonium hydroxide aromatic polymers as AEMFC [10–13]. These membranes were typically prepared by attachment of chloromethyl groups to polymer backbones and followed by quaternization to form ammonium salts. Lu et al. reported poly(arylene ether sulfone) membranes functionalized with quaternary ammonium groups (QAPS) on main chain which has excellent thermal stability, resistance to oxidation, and is stable under alkaline conditions ($pH < 12$) [14–16]. On the one hand research efforts have been aimed at the development of novel aromatic polymers with pronounced hydrophilic/hydrophobic separation by changing of chemical modification using ammonium hydroxide groups on side chain rather than main chain [17–20]. Ueda et al. have reported star-shaped sulfonated block copoly(ether ketone)s having inner hydrophilic segments surrounded by outer hydrophobic segments. The membranes obtained showed relatively good dimensional stability, high bound-water content, and excellent ion conductivity [21]. McGrath et al. also investigated the effect of the different sized hydrophilic block segments in the main chain on the morphology of membranes as well as the relationship between the morphology [22]. Hay and Kim et al. reported polymer membranes containing multi-sulfonic acids on side chain of polymer backbone with better hydrophilic/hydrophobic microphase separation exhibit much better single fuel cell performance [23–25]. Fang et al. reported on mono-quaternary ammonium hydroxide on poly(phthalazinon ether sulfone ketone) anion exchange membrane, which showed high conductivity [26]. We are interesting the structures of tetra-quaternary ammonium hydroxide on phthalazine group, which would provide the better formation of hydrophilic/hydrophobic well-separated channels.

The purpose of this work is to prepare poly(tetraphenyl ether phthalazine) containing tetra quaternary ammonium hydroxide polymer membrane having well-separated hydrophilic/hydrophobic phase. This work is an attempt to synthesize PTPPES containing tetraphenyl groups on a polymer side chain, followed by chloromethylation to prepare tetra-chloromethylated PTPPES. The tetraphenyl rings on side chain of the PTPPES were selectively chloromethylated, and the phenyl rings attached the sulfone groups in main chain were deactivated toward chloromethylation by strong electron-withdrawing groups. These structures provided tetra quaternary ammonium hydroxide per repeating unit that increased the ionic conductivity. The resulting membranes were studied by ^1H NMR spectroscopy, thermogravimetric analysis (TGA), water uptake, ion exchange capacity (IEC), ion conductivity and cell performance.

2. Experimental

2.1. Materials

1,2-Bis(4-fluorobenzoy1)-3,4,5,6-tetraphenyl benzene (BFBTPB) and poly(tetraphenyl ether phthalazine)s were prepared as reported previously (Scheme 1) [27,28]. Commercial bis(4-fluorophenyl) sulfone, bis(4-hydroxyphenyl)sulfone, potassium carbonate, glacial acetic acid, hydrazine monohydrate, zinc chloride ($ZnCl_2$), hydrochloric acid (HCl), paraformaldehyde, 30 wt% trimethylamine aqueous solution, potassium hydroxide, and phenolphthalein were purchased from Sigma–Aldrich Ltd. and used as received. Commercial grade sulfolane, toluene, chlorobenzene, dimethyl sulfoxide (DMSO), were dried overnight over calcium hydride and distilled prior to use. Other Commercially available solvents, such as methanol, acetone, hexane, distilled water were used without further purification.

2.2. Preparation of poly(tetraphenyl ether ketone sulfone) (PTPEKS)

A typical polycondensation procedure follows (Scheme 1): To a 100 mL three necked round bottomed flask, fitted with Dean–Stark trap, condenser, nitrogen inlet/outlet, and magnetic stirrer, monomer 1,2-bis(4-fluorobenzoy1)-3,4,5,6-tetraphenyl benzene (0.8032 g, 1.28 mmol), bis(4-fluorophenyl) sulfone (1.3034 g, 5.12 mmol), bis(4-hydroxyphenyl) sulfone (1.6037 g, 6.40 mmol), K_2CO_3 (1.0614 g, 7.68 mmol), sulfolane (11.0 mL), and chlorobenzene (11.0 mL) were charged. The mixture was refluxed for 3 h at 160–180 °C. After the produced water was azeotroped off with chlorobenzene, the mixture was heated at 210 °C for about 1 h until a highly viscous solution was obtained. The resulting mixture was cooled and then poured into a mixture of methanol (100.0 mL)/water (100.0 mL)/HCl (10.0 mL) to precipitate a white fibrous polymer and then, collected by filtration, and washed with water. The polymer, collected by filtration was dried in vacuum at 80 °C for 24 h. ^1H NMR (400 MHz, DMSO-d_6), δ = ppm: 8.11–7.90 (d, 12 H, 3 ortho $C_6H_2SO_2C_6H_2$), 7.62–7.57 (m, 4 H, ortho $2C_6H_2CO$), 7.33–7.15 & 7.01–6.79 (d, 12 H, 3 meta $C_6H_2SO_2C_6H_2$), 7.01–6.80 (m, 20 H, $4C_6H_5$, 4 H, meta $2C_6H_2CO$), FT-IR: 1710 (C=O stretching), 1249, 1026, 690 (O–S–O stretching) cm^{-1}.

2.3. Preparation of poly(tetraphenyl phthalazine ether sulfone)s (PTPPESs)

A typical intramolecular ring-closure reaction followed (Scheme 1): To a solution of PTPEKS (2.0 g, 3.70 mmol) in chlorobenzene (70.0 mL) and glacial acetic acid (15.0 mL, 0.262 mol) was added hydrazine monohydrate (15.0 mL, 0.304 mol) over a period of 30 min. The cloudy, colorless reaction mixture was heated at 130 °C for 12 h. The resulting