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High efficiency of proton transport by clustering nanochannels in multi-sulfonated propeller-like nonplanar hexaphenylbenzene poly(ether sulfone)s

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ABSTRACT

The propeller-like nonplanar building unit containing poly(aryl ether ketone)s were synthesized from 1,2-bis(4-hydroxyphenyl)-3,4,5,6-tetraphenyl-benzene (BHPTPB) and bis(4-fluorophenyl) sulfone with bis(4-hydroxydiphenyl) sulfone in NMP. New structures and/or morphologies for existing materials need to be considered in case if increased benefits are desired. The sulfonation was taken selectively on hydrophilic block segment as well as para position of the pendent phenyl groups with concentrated sulfuric acid. The stoichiometry mole ratios were changed with hydrophilic blocks of 12, 15, 17, 20, and 23 mol% of BHPTPB monomer to control the ion exchange capacity. The structural properties of polymer membranes (HP-12, 15, 17, 20, and 23) were studied by FT-IR, ¹H NMR spectroscopy, thermogravimetric analysis (TGA), and atomic force microscope (AFM). The water uptakes were 8.1–69.4% at 75 °C with changing the ion exchange capacities. The resulted proton conductivities were 66.58–103.73 mS/cm at 80 °C with 90% relative humidity. The highest power density of a fuel cell using HP-23 and Nafion 211 was 0.47 and 0.45 W/cm², respectively, at 0.6 V.

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1. Introduction

In recent years, enormous advancement has occurred in the development of proton exchange membrane fuel cell (PEMFC), since they play an important role as the power source for vehicles and portable devices. For decades, the perfluorinated sulfonic acid membranes (Nafion and Aciplex) have been used, because they exhibit a unique combination of properties, including excellent chemical stability and high ionic conductivity, and super acid strength [1,2]. Recently, many

research groups have studied as how to overcome the associated drawbacks of Nafion membranes [3–8]. Especially, thermally stable hydrocarbon PEMFC is emerging as candidate membranes, which can be used at elevated temperatures of greater than 100 °C. Poly(ether sulfone)s and poly(ether ketone)s are primarily chosen because they have achieved an excellent position amongst other thermoplastic polymers by virtue of their superior properties such as thermal stability, high heat distortion temperature, chemical inertness, electrical performance, and flame retardancy [9–15].

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Enormous efforts have been carried out to study the modification of the monomer structures and polymer matrix. The resulting hydrocarbon PEMFCs have been classified as fifth generation polymers, which are linear, block, grafting, crosslinked/branched, and inorganic/organic composite polymer membranes [16–19]. Despite the superiority index and the considerable degree of research, the hierarchical structure of the membrane and the mechanism of cation exchange remain poorly understood and those hydrocarbon PEMFCs did not show sufficient results as a replacement to Nafion. To improve proton conductivity, introducing a high content of sulfonation on polymer backbone is necessary but it has a disadvantage of swelling effect that reduces the mechanical properties of the polymer [20,21].

To improve the proton conductivity and cell power, A. S. Hay 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 and size of hydrophilic block segments. These polymer membranes are randomly distributed nanoclusters of 6 or 12 sulfonic acids derived from hexaphenyl-bisphenol monomer with better hydrophilic/hydrophobic microphase separation, exhibiting much better single fuel cell performance [22]. Ueda also reported the sulfonated poly(ether sulfone)s with highly sulfonated units, which possessed excellent hydrophilic/hydrophobic microphase separation, showed higher water uptake and proton conductivity. McGrath reported the preparation of block copolymers, which formed better hydrophobic/hydrophilic phase separation, and provided good proton conductivity [23,24].

Recently, Lambert reported that hexaphenylbenzene molecule, which is a propeller-like nonplanar conformation molecule, is different from the structures of the aforementioned organic molecules owing to the steric effect of the peripheral phenyl rings [25]. The propeller-like conformation enables π – π interaction between the peripheral aromatic rings facing each other, and the resulting sextuple accumulation of the π – π interaction would lead to the so-called “toroidal delocalization” [25–29]. Therefore, the propeller-like conformation has been regarded as one of the promising three-dimensional topologies and is expected to exhibit unique electronic features [28,29]. We propose that new PEMFC containing propeller-like structure would exhibit interesting properties, because the rigid and twisted conformation provides stable dimensional stability and excellent cell performance due to the good hydrophilic/hydrophobic phase separation and wide channels.

In this article, we report our studies on propeller-like nonplanar building unit containing poly(ether sulfone)s, which has four sulfonic acids per monomer unit on the side phenyl groups, and not on the main chain. The characteristics of the reported work were to provide high proton conductivity, excellent mechanical strength and high thermal stability with less water uptake phenomena. The chemical structure of synthesized polymers was investigated, and the synthesized copolymers were characterized by FT-IR, ^1H NMR spectroscopy, thermogravimetric analysis (TGA), GPC, the proton conductivities, water uptake, and ion exchange capacity (IEC), and we also studied the cell performance. The results suggest potential applications of the synthesized polymer as proton exchange membrane fuel cell. The propeller-like nonplanar

tetraphenyl rings in side chain of the SHP were selectively sulfonated, but phenyl rings beside the sulfone groups in main chain were deactivated toward sulfonation by strong electron-withdrawing groups. The sulfonic acid on side chain was expected to provide better clustering effect and hydrophilic/hydrophobic separation, thus improving cell performance.

2. Experimental

2.1. Materials

Zinc powder, TiCl_4 , pyridine, 4-methoxybenzaldehyde, bromine, triethylamine, potassium carbonate, tetraphenylcyclopentadienone, boron tribromide, 4,4'-difluorophenylsulfone, bis(4-hydroxyphenyl)sulfone, sodium chloride, sodium sulfate, sodium hydroxide, hydrochloric acid, and concentrated sulfuric acid were purchased from Aldrich Chemical and used as received. Commercial grade sulfolane, NMP and toluene were dried overnight over calcium hydride and distilled prior to use. Other commercially available solvents such as, tetrahydrofuran (THF), dichloromethane, hexane, acetone, ethanol, methanol, toluene, ethylacetate, dimethylsulfoxide, and water were also used without any further purification.

2.2. Synthesis of 1,2-bis(4-methoxybenzene)-ethylene

Under an N_2 atmosphere, a three-necked flask equipped with a magnetic stirrer was charged with zinc powder (1.6 g, 0.24 mol) and 40 mL of THF. The mixture was cooled to -5 to 0°C , and TiCl_4 (1.3 mL, 0.12 mmol) was slowly added by a syringe by keeping the temperature under 0°C . The suspending mixture was warmed to room temperature and stirred for 0.5 h, then heated at reflux for 2.5 h. The mixture was again cooled to -5 to 0°C , charged with pyridine (0.5 mL, 0.06 mmol) and stirred for 10 min. The solution of 4-methoxybenzaldehyde (24 mmol) in 15 mL of THF was added slowly. After addition, the reaction mixture was heated at reflux until the carbonyl compounds were consumed (monitored by TLC). The reaction was quenched with 10% K_2CO_3 aqueous solution and taken up with CH_2Cl_2 . The organic layer was collected and concentrated. The crude material was purified by flash chromatography to obtain the desired products (Scheme 1).

2.3. Synthesis of 1,2-bis(4-methoxybenzene)-1,2-dibromoethylene

Under an N_2 atmosphere, a three-necked flask equipped with a magnetic stirrer was charged with 1,2-bis(4-dimethoxybenzene)-ethylene (25.7 mmol, 6.17 g) and dichloromethane (200 mL) to which was added a solution of bromine (25.7 mmol, 1.32 mL) in dichloromethane (5 mL). The reaction mixture was stirred under an atmosphere of nitrogen for 30 min and concentrated under reduced pressure to give a white solid. Recrystallization of the solid from hexane resulted in quantitative formation of 1,2-bis(4-dimethoxybenzene)-1,2-dibromoethylene (Scheme 1).

2.4. Synthesis of 1,2-bis(4-methoxybenzene)acetylene

Under an N_2 atmosphere, a three-necked flask equipped with a magnetic stirrer was charged with 1,2-bis(4-dimethoxybenzene)-

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