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Anion conductive tetra-sulfonium hydroxides poly(fluorenylene ether sulfone) membrane for fuel cell application

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ABSTRACT

A series of anion exchange membranes of poly (fluorenylene ether sulfone) containing tertiary sulfonium hydroxide-functionalized fluorenyl groups were synthesized by sequential polycondensation, chloromethylation, substitution with dimethyl sulfide and ion exchange. They showed excellent solubility in polar aprotic solvents. Consequently, flexible and tough alkaline membranes with varying ionic contents were obtained by an anion exchange of tertiary sulfonium chloride polymers with 1.0 M KOH at room temperature. Different levels of substitution were performed to achieve high ionic conductivity as well as upholding the membranes' mechanical stability. The tertiary sulfonium membranes demonstrated lower water uptake compared to quaternary ammonium membrane. High hydroxide ion conductivity was achieved up to 18.3 mS cm⁻¹ at 80 °C with the membrane of the highest ion exchange capacity (IEC, 1.51 mmol g⁻¹). The resulting alkaline polymers were characterized by ¹H NMR, FT-IR, thermogravimetric analysis (TGA), water uptake, IEC, atomic force microscopic (AFM) images.

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Introduction

Fuel cells are widely regarded as one of the most efficient and clean energy sources as alternatives to fossil fuel. They offer many advantages, such as high efficiency, high energy density, quiet operation, and environmental friendliness. Anion-exchange membranes (AEMs) have been used in alkaline polymer electrolyte fuel cell. However, currently commercial AEMs which typically have cross-linked polystyrene backbone are not very stable in high pH environments. Therefore, the

researchers are interested in developing new AEMs that are stable in high pH values and high temperature environment, while maintaining high conductivity and ion selectivity [1–4]. At present, perfluorinated polymer membranes, such as Nafion[®] and Flemion[®] are widely used for PEM materials because of their excellent physical & chemical stability, and high proton conductivity [5–8]. However, they suffer from such disadvantages as limited operation temperature (0–80 °C), high cost, insufficient durability and high methanol permeability. The dependence of platinum catalysts is in

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essence a problem of limited natural resource rather than a matter of price only [9,10].

Alkaline fuel cells have numerous advantages over proton exchange membrane fuel cells on both cathode kinetics and ohmic polarization. APEFCs are designed to provide sufficient hydroxide 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 exchange membranes and to develop the key structure-property relationships for these types of ion-conducting membranes. There have been significant advances in the synthesis of ammonium hydroxide aromatic polymers as alternative to proton exchange membrane [11–15]. However, it is difficult to obtain an ideal balance between high ion conductivity and low water uptake. The membranes containing high quaternary ammonium hydroxide tend to be swelled by water that affects membrane's performance. Hence, it is an urgent need to develop an AEM with adequate anion concentration, while retaining high mechanical strength in any suitable fuel of AEMFC [16].

Watanabe et al. reported anion exchange membrane containing quaternary ammonium hydroxide on fluorenyl group [17]. We have also prepared quaternary ammonium functionalized anion exchange membranes by modification of the chemical structures of fluorenyl polymer. They exhibited high swelling degree and low alkaline stability [18]. However, tertiary sulfonium cation chemically retains both low basicity and ionic strength. Therefore, our interest is about the structures of tertiary sulfonium hydroxide on fluorenyl group, which would provide good mechanical stability and also high ionic conductivity. In addition, we also focus on the comparative study between the membrane properties of the sulfonium alkaline polymers and quaternary ammonium alkaline polymers.

This work is an effort to synthesize PFES-S-OH containing tertiary sulfonium hydroxide substituted fluorenyl groups on a polymer backbone having characteristics of low water uptake and high conductivity. A series of poly(fluorenylene ether sulfone)s were synthesized via condensation polymerization, and followed by chloromethylation using a mixture of chloromethyl methyl ether (CMME), anhydrous zinc chloride (ZnCl_2) as Lewis acid catalyst, and thionyl chloride (SOCl_2) as a catalyst activator within 7 h. Thereafter, tertiary sulfonium cationic group functionalized alkaline fluorenyl membrane was obtained by treating with excess dimethyl sulfide and ion exchange with 1.0 M KOH, respectively.

Experimental

Materials

Bis(4-fluorophenyl) sulfone (99%, 383-29-9), 9,9'-bis(4-hydroxyphenyl) fluorene (97%, 3236-71-3), bis(4-hydroxyphenyl) sulfone (98%, 80-09-1), potassium carbonate ($\geq 99\%$, 584-08-7), zinc chloride (ZnCl_2) ($\geq 98\%$, 7646-85-7), thionyl chloride (SOCl_2) (97%, 7719-09-7), 1,1,2,2-tetrachloroethane ($\geq 98\%$ 79-34-5), chloromethyl methyl ether (CMME) ($\geq 92.5\%$, 107-30-2), dimethyl sulfide ($\geq 99\%$, 75-18-3) and potassium hydroxide (90%, 1310-58-3) were

purchased from Sigma–Aldrich and used as received. Commercial grade *N,N*-dimethyl acetamide (DMAc) and toluene were dried over calcium hydride and distilled prior to use. Other commercially available solvents, such as dimethyl sulfoxide, ethanol, methanol, dichloromethane and acetone were used without further purification.

Preparation of poly(fluorenylene ether sulfone)s (PFES)

A typical polycondensation procedure was followed (Scheme 1): Polymerization reaction was conducted in a 100 mL three-neck round bottomed flask, fitted with Dean–Stark trap, condenser, nitrogen inlet/outlet, and magnetic stirrer. The flask was charged with bis(4-fluorophenyl) sulfone (2.5 g, 9.83 mmol), 9,9'-bis(4-hydroxyphenyl) fluorene (0.69 g, 1.97 mmol), bis(4-hydroxyphenyl) sulfone (1.97 g, 7.87 mmol), potassium carbonate (1.7 g, 12.29 mmol), *N,N*-dimethylacetamide (13.0 mL), and toluene (12.0 mL). The resultant mixture was refluxed for 6 h at 135 °C under nitrogen atmosphere with Dean–Stark trap. After the complete dehydration, the reaction temperature was elevated to 165 °C for about 2 h until a highly viscous solution was obtained. The thus-obtained reaction mixture was cooled to room temperature and then poured into a mixture of methanol-water to precipitate as white fibrous polymer and collected by filtration, and finally washed with water. The polymer was dried in a vacuum oven at 80 °C for 24 h ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ : 8.10–7.94 (m, 12H, 3ortho $\text{C}_6\text{H}_2\text{SO}_2\text{C}_6\text{H}_2$), 7.90–7.81 (m, 2H), 7.49–7.35 (m, 6H), 7.32–7.15 (m, 10H, meta $\text{C}_6\text{H}_2\text{SO}_2\text{C}_6\text{H}_2$), 7.14–7.08 (m, 4H), 7.07–7.05 (m, 2H), 7.00–6.89 (m, 4H). FT-IR: 3100 (aromatic C–H), 1600–1475 (aromatic C=C), 1325 & 1115 (O–S–O), 1250 (aryl ether) cm^{-1} .

Preparation of chloromethylated poly(fluorenylene ether sulfone)s (PFES-Cl)

The chloromethylation reaction of PFES was performed in a 100 mL three necked round bottomed flask, fitted with condenser, nitrogen inlet/outlet, and magnetic stirrer. To a solution of PFES (1.0 g) in 1,1,2,2-tetrachloroethane (6.5 mL), zinc chloride (80 mg) and thionyl chloride (1.0 mL) were added successively at room temperature. Then, chloromethyl methyl ether (10.0 mL) was added dropwise. The resultant mixture was stirred for 7 h at 30 °C. The reaction mixture was poured into methanol-water mixture and washed with a mixture of methanol and deionized water several times. The light brown solid was collected by filtration, and dried in a vacuum oven for 24 h at 80 °C to give PFES-Cl. ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ : 8.10–7.95 (d, 12 H, 3ortho $\text{C}_6\text{H}_2\text{SO}_2\text{C}_6\text{H}_2$), 7.91–7.80 (m, 2H), 7.65–7.38 (m, 4H), 7.35–7.20 (m, 10 H, meta $\text{C}_6\text{H}_2\text{SO}_2\text{C}_6\text{H}_2$), 7.16–6.88 (m, 8H), 4.81 (s, 4H, 2- CH_2Cl), 4.65 (s, 4H, 2- CH_2Cl).

Preparation of sulfonium poly(fluorenylene ether sulfone) chloride (PFES-S-Cl)

PFES-S-Cl was prepared from a solution of PFES-Cl (0.5 g) in DMSO (6.0 mL). First, excess dimethyl sulfide was added dropwise. The mixture was stirred at 70 °C and also dimethyl sulfide was further added twice to complete the formation of

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