Journal of Power Sources 224 (2013) 42–49

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Concentrated sulfonated poly (ether sulfone)s as proton exchange membranes

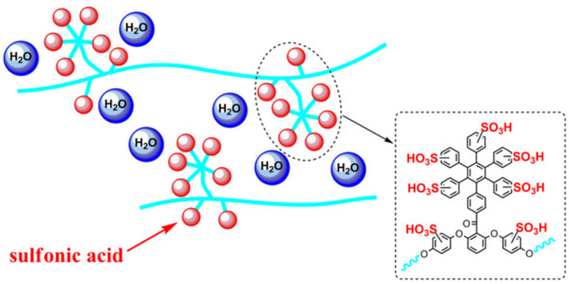
Sinan Feng, Kunzhi Shen, Yang Wang, Jinhui Pang*, Zhenhua Jiang

Alan G. MacDiarmid Institute, Department of Chemistry, Jilin University, No. 2699 Qianjin Street, Changchun 130012, PR China

HIGHLIGHTS

- ► A series of new concentrated sulfonated poly (ether sulfone)s were synthesized.
- ► These polymers own lower activation energy (E_a) of conductivity compared to Nafion.
- ► The membrane with IEC = 1.66 mequiv g^{-1} exhibits higher conductivity than Nafion.
- ► These membranes show considerable water management and proton conductivity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 July 2012
Received in revised form
17 September 2012
Accepted 18 September 2012
Available online 27 September 2012

Keywords:
Sulfonated poly (ether sulfone)s
Proton exchange membrane
Concentrated sulfonation sites
Fuel cells

ABSTRACT

A novel bisphenol monomer containing concentrated electron rich phenyls is synthesized, which provides a locally and densely postsulfonation sites. Based on this monomer, a series of new sulfonated poly (ether sulfone)s (SPESs) are successfully obtained by nucleophilic substitution reaction, followed by postsulfonation using concentrated sulfuric acid. All the polymer membranes are readily prepared by solvent casting and exhibit excellent thermal stability and mechanical properties. As ion exchange capacity (IEC) ranging from 0.98 to 1.66 mequiv g^{-1}, the polymers afford considerable proton conductivity and water absorption. SPES-3 with IEC = 1.66 mequiv g^{-1} shows equal proton conductivity (0.131 S cm^{-1}) to Nafion 117 at 100 °C under fully hydrated state. At low IEC level (IEC = 0.92 mequiv g^{-1}), SPES-1 also exhibits higher conductivity ($>10^{-2}$ S cm^{-1}) than some earlier reported sulfonated random polymers. Their excellent performance is attributed to the internal structure of the polymers, which formed distinct phase separation between hydrophilic and hydrophobic moiety observed by SAXS. A combination of high proton conductivities, moderate water uptake, suitable mechanical properties and low swelling ratios for some of the obtained SPES indicates that they are good candidate materials for proton exchange membranes (PEMs).

1. Introduction

Proton exchange membranes fuel cells (PEMFCs), regarding as a significant efficient and renewable energy resource, have attracted more and more attention in recent years. The advantages of fuel cells are their high efficiency and power/energy density, low temperature operation, rapid start-up time [1,2]. Proton exchange membrane (PEM) is a critical part in PEMFC, which serves as a separator for the reactants, a catalyst support, and provides ionic pathways for proton transport [3]. The perfluorosulfonic acid ionomer membranes, represented by Nafion (a registered trademark of DuPont Co.), are the most commonly used PEMs and have acted as benchmarks for membrane performances due to their excellent chemical and electrochemical stabilities as well as outstanding proton conductivity [4,5]. However, the cost of Nafion remains high because the polymerization process of perfluorinated polymer is complex and must be carried out under harsh conditions such as high temperature and high pressure [6–8]. Moreover, the

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* Corresponding author. Tel./fax: +86 431 85168199.
E-mail address: pangjinhui@jlu.edu.cn (J. Pang).

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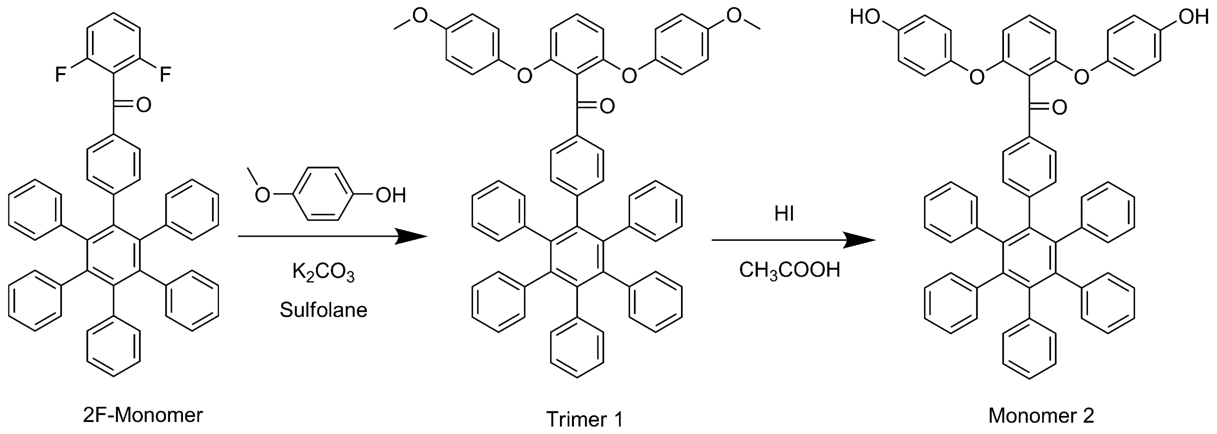
http://dx.doi.org/10.1016/j.jpowsour.2012.09.071



Scheme 1. Synthesis of monomer 2.

mechanical stability and proton conductivity of Nafion can decrease when it is heated over 80 °C, owing to its low glass transition temperature [9,10].

Hence, many arduous efforts are made to exploit an alternative material for PEM. Sulfonated aromatic polymers are supposed to be the most promising candidate for Nafion, considering their well-known oxidative, hydrolytic stability under harsh conditions and many different chemical structures [8]. Despite these advantages, this series of polymer also faces many issues need to be worked out. It is envisaged that the proton conductivities of randomly sulfonated ionomers are too low as compared with Nafion at the same ionic exchange capacity (IEC) level. While higher IEC value results in excessive water content, which is beneficial for proton transportation but a disaster for mechanical property, dimensional stability and durability. And most random SPAE-type membranes formed ambiguously phase-separated microstructures because of their rigid molecular chains and weak hydrophilic/hydrophobic nature [11–14].

Therefore, we should precisely control the position and density of sulfonic acid groups to form well-connected channels for the transportation of hydrated protons [15], and avoid excessive water uptake happens at the same time. Recently, densely sulfonated copolymers have been attracting increasing attention because of the high contrast in polarity between the hydrophilic and hydrophobic units, this promotes the formation of hydrophilic–hydrophobic phase-separated structures [16]. These polymers contain fewer hydrophilic segments at the same level of IEC values with normal sulfonated ones, and relatively more hydrophobic segments endows them good dimensional stability and mechanical properties. Earlier, Ueda et al. reported novel locally and densely sulfonated poly (ether sulfone)s prepared for PEM. These PESs owned efficient proton conduction in a wide range of 30–95% RH at 80 °C, which were comparable with that of Nafion [17]. Hay and co-workers synthesized dendritic multiblock copoly (ether sulfone)s, bearing sulfonated dendritic clusters, that afforded desirable proton conductivity at a level of IEC (0.92–1.26 mequiv g^{-1}) similar to Nafion [18]. It was expected that the large difference in polarity between the densely sulfonated, hydrophilic portions and the hydrophobic portions of the polymer would produce a greater degree of microphase separation, which in turn would lead to well-developed hydrophilic channels and higher proton conduction. While these densely sulfonated polymers were less studied since the complicated monomers were not easy to tailored and synthesized. Additionally, there was little research on how the distribution of concentrated sulfonic acid groups and the density of them influence internal morphology and even conductivity.

Herein, we design a new monomer containing concentrated phenyls pendent group. To make an approach to the formation of water channels in PEM, a series of sulfonated aromatic polymer are obtained based on the new monomer. The densely sulfonic acid groups on pendent chains are expected to aggregate and form continuous hydrophilic domains, which enhances the phase separation between hydrophobic main chain and hydrophilic side chain. Additionally, aromatic backbone architecture endows polymer with superior thermal and mechanical stability. In this study, we aimed at whether concentrated sulfonic groups on pendent chains would be beneficial for proton conduction and dimensional stability. To investigate the detailed property of this polymer, some measurements were implemented and further discussions will be carried out later.

2. Experimental

2.1. Materials

4,4′-Difluorodiphenyl sulfone (DFDPS) and 4,4′-dihydroxydiphenyl sulfone (DHDPS) was purchased from Japan Chemical Industries, Ltd. DHDPS was purified by recrystallization from deionic water. Sulfolane was purified by vacuum distillation. Anhydrous potassium carbonate was dried at 120 °C for 24 h before used. 2,6-Difluoro-4′-(2,3,4,5,6-pentaphenyl phenyl) benzophenone (2F-monomer) was synthesized in our laboratory via several steps. All other organic solvents were obtained from commercial sources and purified by conventional methods.

2.2. Synthesis

The synthetic processes of monomers and polymers are depicted in Schemes 1 and 2 respectively.

2.2.1. Synthesis of trimer 1

To a 50 mL round-bottom three-necked flask equipped with a mechanical stirrer and a Dean–Stark trap, 2F-monomer (6.748 g, 0.01 mol), 4-methoxyphenol (3.104 g, 0.025 mol) and anhydrous potassium carbonate (3.869 g, 0.028 mol) were charged. Afterward, 30 mL of sulfolane and 5 mL of toluene were added into the flask under argon. The reaction was initially carried out at 140 °C for 3 h to remove the water completely. The subsequent polymerization was performed at 210 °C for 6 h. Then the reaction mixture was poured into water, washed with 15% NaOH (aq) and distilled water several times. The crude product was recrystallized from toluene. Mp: 248.2 °C. Mass spectrum (*m*/*z*): 883.4 (100% relative