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Synthesis and Performance of Sulfonated Poly(Arylene ether Sulfone) as Proton Exchange Membrane

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Abstract

A series of novel sulfonated poly(arylene ether sulfone) (SPAES) were prepared by aromatic nucleophilic substitution polycondensation from 4, 4'-dichlorodiphenylsulfone (DCDPS), 3, 3'-disulfonated-4, 4'-dichlorodiphenylsulfone (SDCDPS) and 4-fluorophenyl hydroquinone and characterized by viscosity measurement, FT-IR, ^{1}H-NMR and TG. The SPAES membranes consisting of different ratio of SDCDPS to DCDPS were cast from their solutions. The alternating current (AC) proton conductivity of SPAES membranes were carried on. The values of inherent viscosity ranging from 1.04 to 2.43 dl/g, implying that SPAESs possessed high molecular weight. The results of TG analysis showed SPAESs were thermal stable up to nearly 200 °C. The acid forms (H^+) of SPAES films were tough and ductile with the tensile strength of 61-91 Mpa. The proton conductivity of SPAES films became higher with the increasing content of SDCDPS in chain composition. SPAES with 50% SDCDPS showed the highest proton conductivity of 0.205 S/cm at 80 °C. The water uptake and dimension swelling of SPAES membranes were also measured. At the same time, SPAES showed excellent proton transportation stability when used at high temperature. SPAESs had a higher water uptake than Nafion 115, while experimental IEC of SPAESs in the range of 0.77-1.35 meq/g at 80 °C were very closed to the calculated ones.

Keywords: Sulfonated Poly(Arylene ether Sulfone); Proton Conductivity; IEC; PEM

1 Introduction

PEMFCs convert chemical energy directly into electrical energy using a series of electrochemical redox reactions which attract considerable attentions as candidate for alternative and clean power sources. Some polymers such as Nafion (DuPont) and Dow (Dow) are successfully commercial polymers for PEMFC because of their chemical stability and high proton conductivity. However, Nafion shows some disadvantages including operating temperature no higher than 80 °C, diffusing

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in high methanol, CO poisoning and high cost limit wider and further researches on them [1]. It is a challenge to drive the investigation of alternative materials.

Poly(arylene ether sulfone)s (PAESs) as a kind of high performance polymers, have been widely applied in many fields such as aerospace, microelectronic because of their excellent thermal, mechanical stabilities [2]. Thus, many researches are currently engaged in synthesizing of sulfonated poly(arylene ether sulfone) (SPAES) which can be one of promising polymers used as proton exchange membrane. Generally, sulfonated poly(arylene ether sulfone) could be prepared by the direct copolymerization method and post-sulfonation method [3]. The sulfonated monomer is needed for the direct copolymerization method. The post-sulfonation method could be carried out by sulfonation of polymers, but some limitations such as low molecular weight, out of control and undesirable side reactions are of concern [4].

In this study, we firstly synthesized SPAESs form DCDPS, SDCDPS and 4-fluorophenyl hydroquinone successfully by synthesising sulfonated monomer (SDCDPS) in advance. SPAES membranes were received by solution casting. The proton conductivities of these membranes were studied.

2 Experimental

2.1 Materials

Fuming sulfuric acid (50%) (Alfa), anhydrous potassium carbonate (Alfa), toluene, dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and N, N-dimethyl acetamide (DMAC) (Shanghai Medicine Group Chemical Reagent Co., Ltd), 4, 4'-dichlorodiphenylsulfone, hydrochloric acid, sodium chloride (Sinopharm Chemical Reagent Co., Ltd) were used as received.

2.2 Synthesis of the 4-fluorophenyl Hydroquinone

4-fluorophenyl hydroquinone was synthesized from p-benzoquinone, 4-fuoroaniline in a three-step synthesis according to the previous report [5, 6]. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.45∼7.42(m, 2H), 7.19∼7.15(m, 2H), 6.85(s, 1H), 6.76∼6.72(m, 2H), 4.68(s, 1H), 4.48(s, 1H).

2.3 Synthesis of the 3, 3'-disulfonate-4, 4'-dichlorodiphenylsulfone (SDCDPS)

3, 3'-disulfonate-4, 4'-dichlorodiphenylsulfone was synthesized from fuming sulfuric acid(50%) and 4, 4'-dichlorodiphenylsulfone according to the previous report [7]. ^{1}H-NMR of SDCDPS ($CDCl_3$, δ, ppm): 7.34-7.35(d, 2H), 7.87(d, 1H), 7.85(d, 1H), 7.68-7.66(d, 2H).

2.4 Synthesis of Sulfonated poly(arylene ether sulfone)s (SPAESs)

As shown in the Scheme 1, SDCDPS, DCDPS (combined total 1 mmol) and 1 mmol 4-fluorophenyl hydroquinone, 1.2 mmol K_2CO_3, 30 ml DMAC and 12 ml toluene were added into a 100 ml three-neck round bottom flack equipped with a Dean-stark trap, a nitrogen inlet and a thermometer.