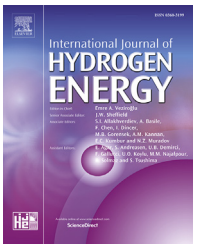
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–7

Available online at www.sciencedirect.com

ScienceDirect

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



Synthesis and characterization of polymer electrolyte membrane containing methylisatin moiety by polyhydroalkylation for fuel cell

Taewook Ryu, Hohyoun Jang, Faiz Ahmed, Nasrin Siraj Lopa, Hanmo Yang, Sujin Yoon, Inhwan Choi, Whangi Kim *

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

ARTICLE INFO

Article history:
Received 20 July 2017
Received in revised form
15 December 2017
Accepted 20 December 2017
Available online xxx

Keywords:
PEM
Super acid
Sulfonation
Dimensional stability
Proton conductivity
Carbon-carbon linkage

ABSTRACT

High molecular weight polymer containing *N*-methylisatin was synthesized by superacid-catalyzed polyhydroxyalkylation reactions. Their functionality with sulfonic acid groups and the measurement of apposite parameters for proton exchange membranes (PEMs) were described. Sulfonic acid groups were introduced into the polymer through sulfonation reaction with chlorosulfonic acid. The membranes were casted from the solution of sulfonated polymer in dimethylsulfoxide (DMSO). The structural properties of the synthesized polymers were investigated by ^{1}H NMR spectroscopy. The membranes were studied by thermogravimetric analysis (TGA), ion exchange capacity (IEC), water uptake, dimensional stability and proton conductivity assessment. Different levels of sulfonation and ion exchange were tested; the resulting membranes exhibited high proton conductivities of up to 88.63 mS/cm. The sulfonated membranes showed good dimensional stability owing to having all carbon-carbon linkages on polymers' backbone.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Polymer electrolyte membrane fuel cell (PEMFC) can efficiently generate high power densities, thereby making it an attractive technology for automobile and portable applications. At present, perfluorinated polymer membranes, such as Nafion® and Flemion®, are widely used for PEM materials because of their excellent chemical & physical stability, and high proton conductivity [1–4]. However, they have some unfavorable properties of high methanol permeability which limits their use in direct methanol fuel cells and also poor performance at temperatures over 100 °C. Nevertheless, their characteristics are derived from fluoro atoms and carbon-carbon bonded chemical structure which attribute relatively long lifetime compared to hydrocarbon membranes. Most hydrocarbon membranes are generally lower ionic conductivities at comparable ion exchange capacities than Nafion [5,6] and more susceptible to oxidative or acid-catalyzed degradation than Nafion by structural ether linkage [7–9]. Chemical degradation of membranes is generally thought to play the most important role for abating fuel cell performance. Research in the field of hydrocarbon membranes has made great strides throughout the years. Performances of hydrocarbon membranes, such as proton conductivity, power density etc. are close to those of perfluorinated sulfuric acid

* *Corresponding author.*
E-mail address: wgkim@kku.ac.kr (W. Kim).

https://doi.org/10.1016/j.ijhydene.2017.12.164

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Please cite this article in press as: Ryu T, et al., Synthesis and characterization of polymer electrolyte membrane containing methylisatin moiety by polyhydroalkylation for fuel cell, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2017.12.164

membranes, and also their cost is lower. However, the durability of hydrocarbon membranes is not as high as that of Nafion. To overcome this fundamental drawback, the carbon-carbon backbone structured polymers are studied [10–14].

Sulfonated poly (p-phenylene)s and their derivatives are generally synthesized by Ni-catalyzed coupling copolymerization. The carbon-carbon bonded polymers were prepared by Diels-Alder polymerization as well [11–13]. These cabon-carbon backbone based polymer membranes have excellent chemical stability and good performances [15]. But, they are very expensive regarding the processing of monomers, catalyst, and demanding reaction conditions. Since Olah and co-workers explain the high reactivity of electrophilic species in superacid, numerous reactions have already been carried out using superacids as a reaction medium [16,17].

Our aim is to prepare the carbon-carbon linked polymer in main chain without ether group and additionally isatin moieties for improving chemical stability and good solubility in polar solvent. This work is an attempt to synthesize polymer from *N*-methylisatin and biphenyl using trifluoromethane sulfonic acid as a superacid followed by sulfonation with chlorosulfonic acid to prepare sulfonated polymer. The sulfonated polymer membranes were studied by the measurements of ion exchange capacity (IEC), water uptake, and proton conductivity.

Experimental

Materials

Chlorosulfuric acid, isatin, methyl iodide and anhydrous potassium carbonate were purchased from Aldrich and trifluoromethanesulfonic acid (TFSA) from Alfa Aesar. Commercially available solvents, such as acetonitrile, dichloromethane, ethyl ether, methanol and ethanol were also used with or without further purification.

Synthesis of N-methylisatin

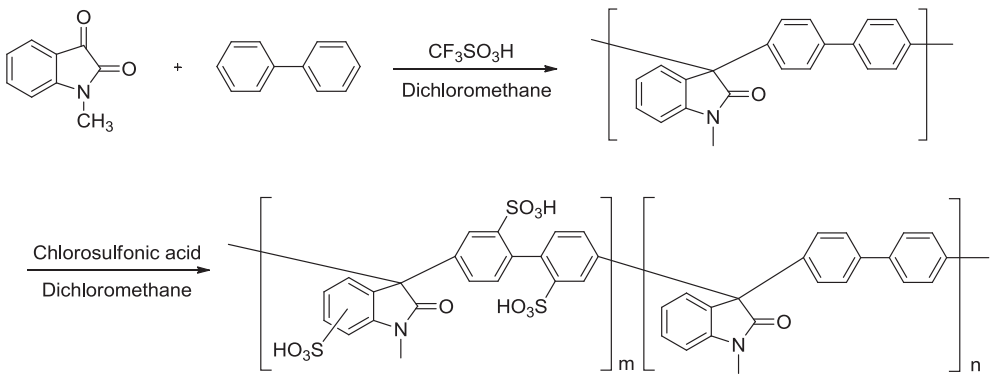
To an 250 mL three-necked round-bottom flask, equipped with condenser, nitrogen inlet and magnetic stirrer, isatin (3.0 g, 20.39 mmol), potassium carbonate (3.38 g, 24.47 mmol), methyl iodide (3.47 g, 24.47 mmol) and acetonitrile (50 mL) were prepared. The mixture was refluxed at 82 °C for 24 h and it was cooled at room temperature. The filtrate was evaporated under reduced pressure and dissolved in ethyl ether (50 mL) to remove potassium carbonate. The reaction mixture was filtered and evaporated to afford a crude *N*-methyl- isatin. After purification by recrystallization using ethanol (80 mL), 2.85 g (95%) a red solid material was obtained and dried in vacuum oven at 60 °C. ^{1}H NMR ($CDCl_3$, ppm, δ): 3.29 (s, 4H, –N–CH_3), 6.92–7.48 (m, 4H, ArH). FT-IR: 3040–3060 (aromatic C–H), 2930–2880 (–CH_3 stretch), 1720 (C=O), 1600–1450 (aromatic C=C), 1260 (C–N) cm^{-1}.

Preparation of poly(phenylene) (PP) and sulfonated poly(phenylene) (SPP)

A typical polyhydroxyalkylation procedure was as follows (Scheme 1): TFSA (8.8 mL) was added to an ice-cooled mixture of *N*-methylisatin (1.63 g, 10.09 mmol), biphenyl (1.56 g, 10.09 mmol) and dichloromethane (4.9 mL) in a 100 mL two-necked round-bottomed flask equipped with a mechanical stirrer. Thereafter, the temperature was raised to 20 °C over a period of 30 min and reaction was continued at this temperature for 15 h to afford a highly viscous dark-green solution. The resulting mixture was decanted dropwise into methanol (400 mL) and washed several times with methanol and water respectively. After drying well, white fiber like poly (phenylene) was obtained (η_{inh} = 0.89 dL/g in NMP at 30 °C). Chlorosulfonic acid (2.7 mL, 40.35 mmol) was added dropwise to a solution of polymer (1.5 g, 5.05 mmol) in dichloromethane (30 mL) at 0 °C for about 30 min. The reaction mixture was stirred for 2 h 30 min at room temperature. The resulting mixture was poured slowly into distilled water and the precipitate was washed several times with water until the residual water was pH neutral, and finally dried under vacuum at 80 °C for 24 h to give a sulfonated poly (phenylene). FT-IR: 3600–3200 (–OH), 3040–3060 (aromatic C–H), 2950–2850 (–CH_3 stretch), 1600–1475 (aromatic C=C), 1720 (C=O), 1325 & 1115 (O–S–O), 1260 (C–N) cm^{-1}.

Membrane preparation and characterization

The copolymer structure was confirmed by Fourier transform infrared (FT-IR) spectroscopy using a NICOLET FT-IR spectrometer with thin homogeneous polymer cast film. And also it was confirmed by ^{1}H NMR spectra recorded on a Bruker DRX (400 MHz) spectrometer using DMSOd_6 as a solvent and



Scheme 1 – Preparation of poly(phenylene) and sulfonated poly(phenylene).

Please cite this article in press as: Ryu T, et al., Synthesis and characterization of polymer electrolyte membrane containing methylisatin moiety by polyhydroalkylation for fuel cell, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2017.12.164

Download English Version:

https://daneshyari.com/en/article/7707448

Download Persian Version:

https://daneshyari.com/article/7707448

Daneshyari.com