



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

A novel proton conducting polymer functionalized with 1-hydroxy-benzimidazole-3-oxide

S. Akay Sazaklioglu ^{a,1}, B. Esat ^{a,*}, D. Vladikova ^{b,2}, I. Genov ^{b,3},
E. Mladenova ^{b,4}

^a Fatih University, Department of Chemistry, Buyukcekmece 34500, Istanbul, Turkey

^b Bulgarian Academy of Sciences, Acad. Evgeni Budevski Institute of Electrochemistry and Energy Systems (IEES), Sofia, Bulgaria

ARTICLE INFO

Article history:

Received 15 December 2015

Received in revised form

22 March 2016

Accepted 20 May 2016

Available online xxx

Keywords:

Membrane

Polymer

Electrolyte

Fuel cell

1-Hydroxy-benzimidazole-3-oxide

ABSTRACT

Proton-exchange membrane fuel cells (PEMFCs) use the chemical reaction between hydrogen and oxygen to produce electricity. There are some main technical problems associated with the common operation temperature of PEMFCs which is about 80 °C such as catalyst poisoning and low activity, flooding of the electrode due to the water, which is necessary to ensure proton conductivity of the polymer electrolyte membrane. Several approaches are developed for overcoming the complications. A promising approach is the development of new polymeric systems which can work at elevated temperatures (above 120 °C). There is a great need to develop new systems appropriate for operation temperatures above 150–160 °C. This study presents the first results obtained for the proton conductivity of a 1-hydroxy-benzimidazole-3-oxide (HBNN)-functionalized polymer (SBNN) which is stable up to 240 °C without thermal decomposition.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Proton-exchange membrane fuel cells (PEMFCs) are promising power generators which use the chemical reaction between hydrogen and oxygen to produce electricity and heat and water as waste product. They can be applied in transport for electrically powered vehicles, as well as for distributed power generation, combining zero emission, low noise and high

efficiency. The common operation temperature of PEMFCs is about 80 °C. The main technical problems at that operation temperature are: poisoning and low activity of the catalyst, flooding of the electrode due to the water, which is necessary to ensure proton conductivity of the polymer electrolyte membrane [1,2]. Several approaches are developed for overcoming the complications such as increase of the catalyst activity and stability towards poisoning [3], optimization of the electrode structure [3–5], development of gas diffusion

* Corresponding author. Tel.: +90 212 866 33 00.

E-mail addresses: sevdaakay07@gmail.com (S. Akay Sazaklioglu), besat@fatih.edu.tr (B. Esat), d.vladikova@bas.bg (D. Vladikova), dedfin45@abv.bg (I. Genov), emiliya@bas.bg (E. Mladenova).

¹ Tel.: +90 212 866 33 00.

² Tel.: +359 2 971 47 33.

³ Tel.: +359 2 971 47 33.

⁴ Tel.: +359 2 971 47 33.

<http://dx.doi.org/10.1016/j.ijhydene.2016.05.185>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

layers which can reduce the flooding with water [6]. However, there is still need of strong research. Another promising approach is the development of new polymeric systems which can work at elevated temperatures (above 120 °C). Those operation conditions have a combined positive effect in respect to: reduced sensitivity towards catalyst poisoning, improved thermal and water management, increased reaction rates at the electrodes and proton conductivity of the electrolyte [7–9]. Different high temperature electrolytes are studied [1,10–14]. The common problem is durability and lifetime. Although the phosphoric acid-doped polybenzimidazole is accepted as one of the most promising systems [1,15–18], it is worth to develop new systems appropriate for operation temperatures above 150–160 °C.

1-hydroxy-benzimidazole-3-oxides (HBNNs) are precursors to the benzimidazole-3-oxide-1-oxyl radicals (BNNs) investigated as building blocks of organic magnetic materials [19–27]. HBNNs have been also tested for their antifungal activities [28]. These compounds have been known to show strong H-bonding intermolecular interactions as evidenced by their insolubility in many organic solvents, high melting points and their IR spectra which show very broad O-H bond stretching vibrations [19,27]. Also, their solubility in aqueous basic solutions indicates the presence of acidic, exchangeable protons.

Hydrogen bonding can be regarded as the incipient state of a proton transfer process and this is true for strong as well as weak hydrogen bonds (H-bonds). However, only for strong H-bonds do such proton transfer occur with significant rate. Since HBNNs exhibit strong H-bonding intermolecular interactions due to presence of acidic and exchangeable N-OH protons, and thermal stability of the polymer synthesized by our group with pendant HBNN groups, a motivation toward the proton conductivity studies of polymers with pendant HBNN functional groups has arisen. This study presents the first results obtained for the proton conductivity of a 1-hydroxy-benzimidazole-3-oxide (HBNN)-functionalized polymer (SBNN).

Experimental

Materials and methods

The reagents have been obtained from Sigma-Aldrich, Merck, J.T. Baker and Acros Organics. All chemicals were used as received. 4-Benzyloxybenzaldehyde polystyrene HL (Catalogue #-855026) was purchased from Merck-Novabiochem and used as supplied in the synthesis of the SBNN polymer.

Perkin Elmer BX for FTIR-ATR instrument was used for FTIR spectrum of synthesized intermediates.

For ^1H and ^{13}C spectrums of other molecules were used CDCl_3 and DMSO-d_6 . All measurements were carried out at room temperature by using Bruker Avance 400 MHz NMR spectrometer.

All TGA data were obtained using 2–5 mg of sample, under nitrogen flow, 10 °C/min heating rate, between to 25 °C up to 700 °C and by using Perkin Elmer Instruments model STA 600 device.

The determination of percentages of C,H,N,S elements in the polymer structure was performed with the FLASH 2000 Organic Elemental analyzer.

The proton conductivity of the functionalized HBNN polymer was studied by Electrochemical Impedance Spectroscopy (EIS) [29] performed on symmetrical electrolyte supported button cells with silver electrodes deposited by slurry coating. The technique ensured separation of the bulk resistance from the contribution of the interface phenomena (electrode/electrolyte, as well as grain boundaries in the electrolyte which is obtained by hot pressing of polymer particles). The conductivity can be calculated using the following expression:

$$\sigma = L/A R_b \quad (1)$$

where σ is the conductivity (Scm^{-1}), L is the sample thickness (cm), A is the electrode area (cm^2) and R_b is the bulk resistance extracted from the high frequency part of the impedance spectrum.

Since the main goal was to check the existence of proton conductivity in the produced polymer (SBNN), which should be a basis for further improvements, we have used the most simple approach for preparation of measurable samples - hot pressing at 120–140 °C of the synthesized polymer which is in the form of small ball-shaped particles at pressure of 1 ton for 5 min, i.e. no procedure for production of thin membrane has been developed. Those conditions ensured relatively stable pellets with dimensions: diameter 10 mm and thickness in the range 1–2 mm. For comparison with the commonly applied PEMFC electrolyte Nafion, the same procedure was applied for the fabrication of pellets from solid Nafion particles.

The impedance measurements were carried out on Solartron 1260 FRA in the frequency range 1 MHz – 0.1 Hz with density 5 points/decade, using potentiostatic mode and amplitude of the AC signal 1 V in appropriate atmosphere – air, nitrogen, dry and wet (3%) hydrogen at room temperature.

Synthesis of HBNN polymer

There are several different literature methods known for the synthesis of HBNN molecules. The most commonly used ones are the condensation of nitroso benzene and benzonitrile [30,31], condensation of nitron and benzofuroxans [32], and condensation of *ortho*-benzoquinone dioxime and aldehyde [33]. In this study, condensation of *ortho*-benzoquinone dioxime and aldehyde was used (Fig. 2). *Ortho*-benzoquinone dioxime was synthesized by the reduction of benzofuroxans using semicarbazide hydrochloride (Fig. 1) [34].

Synthesis of 1-azido-4-methyl-2-nitrobenzene (1)

3.04 g of 4-methyl-2-nitroaniline was added to 9 ml $\text{H}_2\text{O}/5$ ml HCl mixture in an ice-salt bath maintained at -10 °C. 9: 5 (v/v) HCl mixture was added dropwise until a clear solution was obtained. The mixture was allowed to stir for 1 hour and then a solution of 1.452 g NaNO_2 dissolved in 5 ml water was added. The reaction mixture was allowed to stir for another hour and filtered. To the filtrate, 1.3 g NaN_3 in 5 ml water was added and it was allowed to stir for 1 hour. The precipitate was collected by filtering, washed twice with the mother liquor and then twice with 30 ml cold water. The solid was left to dry under

Download English Version:

<https://daneshyari.com/en/article/7710172>

Download Persian Version:

<https://daneshyari.com/article/7710172>

[Daneshyari.com](https://daneshyari.com)