Energy 94 (2016) 292–303

Contents lists available at ScienceDirect

Energy

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

Study of hydrogen crossover and proton conductivity of self-humidifying nanocomposite proton exchange membrane based on sulfonated poly (ether ether ketone)

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ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form
25 September 2015
Accepted 14 October 2015
Available online 21 November 2015

Keywords:
Proton conductivity
Hydrogen crossover
Self-humidifying nanocomposite membrane

ABSTRACT

Fuel crossover and proton conductivity in proton exchange membranes have considerable effects on the performance of polymer electrolyte membrane fuel cells. In the present study, a self-humidifying nanocomposite membrane based on SPEEK (Sulfonated poly ether ether ketone) and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported Pt catalyst was prepared and its hydrogen crossover and proton conductivity were investigated. Hydrogen crossover was evaluated by LSV (linear sweep voltammetry) as a function of temperature, RH (relative humidity) and hydrogen partial pressure. Design of experiments by RSM (response surface methodology) was used for investigating the effects of the related parameters. Increasing each of the parameters leads to increase the gas crossover. In addition, the proton conductivity was measured by EIS (electrochemical impedance spectroscopy) as a function of temperature and relative humidity and a mathematical relationship was obtained based on the experimental data. Note that all of the mentioned tests were performed on Nafion117 membranes in order to compare the obtained results. Then, performance of the both membranes was compared based on TPI (transport performance index) at the end. The results show that in the same operating conditions, the value of TPI in the SPEEK nanocomposite membrane was less than that of Nafion117. Therefore, the self-humidifying SPEEK membrane shows a better performance in transport properties.

1. Introduction

PEMFCs (proton exchange membrane fuel cells) are promising alternative energy conversion devices for both portable and stationary applications due to their high energy conversion efficiency and environmental benefits. They have some advantages with respect to other types of fuel cells e.g., high power density and low operating temperatures (compared to other fuel cell types such as the SOFC which its operating temperature is approximately 700 °C) [1–3]. In order to improve performance of the PEM (proton exchange membrane) fuel cells and to reduce various irreversible losses that occur during operation of the fuel cell, many significant researches have been devoted to PEM fuel cells, including mathematical modeling, performance and energy analyses in power generation and auxiliary systems, water and thermal management, development of new membranes, electrocatalysts and a lot of experimental investigations [4–10]. The heart of a typical PEM fuel cells is its proton exchange membrane (PEM) which separates the catalyzed cathode and anode electrodes. To achieve a high efficiency, the membranes must possess properly high proton conductivity, low electron conductivity, adequate mechanical and chemical stability under operating conditions, low fuel or oxygen by-pass, good balance of water transfer, good transfer of gases to the catalyst layer and etc. [11,12]. The ability of the membrane to transfer the protons to cathode side is one of the most overriding factors in determination of the amount of current generated, and this parameter itself depends on membranes humidity, temperature, membrane thickness and etc. [13]. EIS (electrochemical impedance spectroscopy) is the most applicable method to reach proton conductivity. A more recent work by Xiaozi Yuan et al. has reviewed PEM fuel cells using EIS technique [14]. The structure and physical properties of different membrane systems such as proton conductivity have been compared in a review paper by Smith et al. [11].

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http://dx.doi.org/10.1016/j.energy.2015.10.048
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The diffusion of reactants through the membrane lowers the fuel cell efficiency due to different phenomena. In PEM fuel cells, transmitted oxygen (hydrogen) occupies some catalytic sites at the anode (cathode) side, reacts with hydrogen (oxygen) at the presence of oxygen (hydrogen) and generates some heat and water without generating any current. Also, oxygen crossover produces peroxide and hydroperoxide radicals which accelerate the chemical and then mechanical degradation of the membrane. Still, in the fuel cells which the cathode is fed with air, permeation of nitrogen gas, leads to local lack of fuel in the anode flow field and this phenomena leads to carbon corrosion at the cathode [15]. As reviewed by Ito et al. [16], gas permeability through a membrane can be estimated using several measurement techniques, such as electro-chemical monitoring and time-lag techniques, positron annihilation, volumetric and gas chromatography methods and lifetime spectroscopy. The electrochemical monitoring technique, which monitors current over time for the diffusion-limiting condition through the membrane, has been widely used to characterize the rate of gas permeation. A number of factors are known to affect the hydrogen crossover and proton conductivity, such as the operating temperature, RH (relative humidity), gas pressure, and membrane thickness [17].

The membranes developed so far can be classified into three groups: (1) modified perfluorinated membranes based on perfluorosulfonic acid (PFSA), membranes, which are swelled with nonvolatile solvents or rather incorporate hydrophilic oxides and solid inorganic proton conductors; (2) alternative sulfonated polymers and their composite membranes, such as sulfonated polysulfone (sPSF), Sulfonated poly ether ether ketone (SPEEK), polybenzimidazole (PBI), and polyvinylidene fluoride (PVDF); and (3) acid-base polymer membranes, such as phosphoric acid-doped Nafion-PBI composite membranes [18–22]. PFSA membranes like Nafion are a suitable choice for fuel cell applications and have been used in most of the industrial fuel cell products till now. They have high proton conductivity and mechanical and chemical stability. However, their synthesis process is so complicated and the overall usage cost is expensive [23,24].

SPEEK (sulfonated poly ether ether ketone) is a nonfluorinated membrane with a proton conductivity lower than Nafion. This membrane possesses low cost and excellent thermal, mechanical, chemical and oxidative stability due to its aromatic structure [25]. The proton conductivity of SPEEK membranes as a function of temperature, in different humidities, was reported in the literature [26,27]. SPEEK and Nafion membranes need humidified gases to achieve high proton conductivity. So, they need complicated and heavy humidification devices and cannot be appropriate for portable applications. Therefore most of the researchers attitude to fabrication of self-humidifying membranes. These type of membranes consume permeating reactants in the bulk of the membrane and in this way reduce the amount of crossed over gas [13].

In the present study, the self-humidifying nanocomposite membrane was fabricated based on SPEEK and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported Pt catalyst ($Pt-Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst or $Pt-Cs_{2.5}$). The hydrogen crossover and proton conductivity in different conditions were investigated. A design of experiment (DOE) was done using RSM (response surface methodology) as a tool for determining the experimental points of temperature (T), RH (relative humidity) and hydrogen partial pressure (P_{H2}), analyzing the evaluated data and to provide extensive graphs to highlight the relationship of input parameters with outgoing responses. This methodology has been employed in so many papers of different fields [1,28–35]. The hydrogen crossover was monitored electrochemically using linear sweep voltammetry (LSV) technique at different T, RH and P_{H2}. Its proton conductivity was evaluated and a mathematical equation was obtained for SPEEK/$Pt-Cs_{2.5}$ nanocomposite membranes from the experimental data. The same experiments was conducted on Nafion-117 and the obtained results were compared with SPEEK/$Pt-Cs_{2.5}$.

2. Experimental

2.1. Material

Aromatic polymer poly(oxy-1,4-phenyleneoxy-1,4-phenylene carbonyl-1,4-phenylene) (PEEK) was obtained from Sigma-Aldrich Co. with Mn = 10300, Mw = 20800, density of 1.3 g/mL at 25 °C and melting point of 322 °C. The membrane solvent, i.e. N, N-dimethyl acetamide, was purchased from Merck Co. with the purity of 99%. 12-tungstophosphoric acid ($H_3PW_{12}O_{40}.29H_2O$) as a heteropolyacid material with high purity (cryst. extra pure, 99%), while cesium carbonate salt (Cs_2CO_3), chloroplatinic acid hexahydrate and ($H_2PtCl_6.6H_2O$) with 99% purity were all received from Merck Co. The double-distilled deionized water used in all experiments was prepared with Millipore Milli-Q system.

2.2. Preparation of SPEEK based self-humidifying nanocomposite membranes

Sulfonation of PEEK was carried out in a three neck flask with a stirrer bar. About 250 mL of 95–98% H_2SO_4 (purchased from Merck Co.) was transferred to a reaction flask and heated over an oil bath up to 50 °C under N_2 atmosphere. Then, 12.5 g of PEEK was slowly added under stirring. The polymer was completely dissolved in 1 h and the reaction was continued for another 7 h. After the sulfonation was completed, SPEEK was isolated by precipitation in ice-cold water while stirring, and the precipitated SPEEK was washed thoroughly with DI (deionized) water until reaching a neutral pH, and then stirred overnight to remove the residual acid. The polymer was dried at 60 °C for 12 h followed by overnight drying at 110 °C under vacuum [36–38].

For preparation of the self-humidifying nanocomposite membrane, the SPEEK ($DS_{opt} = 65.12\%$) was dissolved in DMAc at 45 °C to prepare a 10 wt.% solution. In this temperature, the SPEEK polymer was completely dissolved after 1 h. Prior to incorporation of the catalyst particles into the SPEEK matrix, the polymer solution was filtered through a 125 mm size Whatman filter to obtain the clear membrane solution.

$Pt-Cs_{2.5}$ catalyst was synthesized by a titration method [25]. For this purpose, an aqueous solution of $H_2PtCl_6.6H_2O$ (0.04 M, 15 mL) was added drop-wise to an aqueous solution of $H_3PW_{12}O_{40}$ (0.08 M, 44 mL) at 50 °C to obtain a yellow solution. This solution was stirred by a magnetic stirrer with moderate stirring rate. Then an aqueous solution of Cs_2CO_3 (0.12 M, 36 mL) was added drop-wise to the mixture with a volume rate of 0.6 L/min at vigorous stirring and temperature of 50 °C. Then, the resulting milky solution was stirred under moderate stirring rate over-night at room temperature. Finally, the milky solution was evaporated at 50 °C in a conventional oven to solidify and then reduced by H_2 gas at 200 °C for 3 h to reduce the platinum ions to metallic form. Then 15 wt.% of $Pt-Cs_{2.5}$ catalyst was added to the polymer solution and stirred with a magnetic stirrer for 4 h to obtain the homogenous polymer-catalyst solution. For further stirring of the polymer-catalyst solution, this mixture was vigorously sonicated with ultrasonic homogenizer (Sounopuls, HD2200) for 30 min. The obtained solution was cast onto a petri-dish and then put at 60 °C for 12 h followed by further drying at 120 °C under vacuum. The thickness of the nanocomposite membrane was controlled by mild membrane drying and measured by a digital micrometer provided by Mitutoyo. The obtained membrane thickness was about 45 ± 5 μm. Furthermore, for comparison with commercial membranes, Nafion117 membrane was supplied from Electrochem company.