Electrochimica Acta 232 (2017) 226–235

Contents lists available at ScienceDirect

Electrochimica Acta

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

Development of a Crosslinked Pore-filling Membrane with an Extremely Low Swelling Ratio and Methanol Crossover for Direct Methanol Fuel Cells

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ARTICLE INFO

Article history:
Received 11 September 2016
Received in revised form 16 February 2017
Accepted 16 February 2017
Available online 20 February 2017

Keywords:
Fuel cell
Pore-filling
Methanol crossover
Epoxy resin
Proton exchange membrane

ABSTRACT

A poly (ether sulphone)-based pore-filling membrane was successfully fabricated and tested against a conventional Nafion-based membrane in direct methanol fuel cells. An amino-containing polymer with a low degree of sulphonation (DS) was synthesized and used as the supporting substrate. The porous substrate was prepared by introducing the porogenic agent (tetrafluoroborate) into the membrane casting solution. The effects of the content of the porogenic agent on the pore morphologies were evaluated using field emission scanning electron microscopy. Then, an epoxy resin was introduced into the porous electrolyte for the first time to minimize the swelling and methanol crossover that resulted from the high degree of sulphonation. In essence, solidification of the amino groups in the substrate results in 3D crosslinking of epoxy resins, which greatly suppresses the swelling and methanol crossover of the composite membranes with enhanced mechanical properties and enhances the thermal and oxidation stability compared to Nafion 117. The resulting composite membrane also shows high proton conductivity that is only slightly lower than that of Nafion 117. However, the selectivity between the proton conductivity and methanol permeability is higher for the composite membranes than that of Nafion 117. The composite membrane also shows a better performance in single cell tests with 10 M methanol.

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1. Introduction

Direct methanol fuel cells (DMFCs) can convert chemical energy into electrical energy. As a type of potential future power device, they have attracted significant attention because of their light weight, high fuel utilization efficiency, high energy density, low emission, and portability [1–5]. The proton exchange membrane (PEM), which acts as an electrolyte to transport protons from the anode to the cathode and prevent fuel leakage, is the key component in a fuel cell assembly [2,5,6]. For the fabrication of a PEM, various perfluorinated, partially perfluorinated, or sulphonated wholly aromatic polymers (such as polyetheretherketone, polyethersulphone, polybenzimidazoles and polyphenylene oxide) are commonly used and have been thoroughly characterized in terms of their proton conductivity, mechanical properties, swelling and chemical resistance [7–10]. Currently, perfluorinated ionomers (such as Nafion) have become the most widely used PEM materials due to their high proton conductivity as well as acceptable chemical and electrochemical stability. However, the further use of the perfluorosulphonic acid membrane is hindered due to its well-known drawbacks, including its high cost, slow anodic reaction kinetics, limited durability, high degree of water swelling, and most importantly, undesirable methanol crossover, which causes fuel waste and contamination of the platinum catalyst on the cathode side [11–13]. To minimize fuel crossover, a low methanol concentration (less than 2 M) has been used, lowering the fuel efficiency and causing a potential loss at the cathode [14]. These factors have impacted the energy density of DMFCs compared to Li-ion batteries. To develop a larger power density (to compete with Li-ion batteries) and at the same time considering the importance of water in the proton conductivity efficiency of the membrane, the concentration of methanol must be approximately 10 M (32% weight ratio) in aqueous solution [14,15]. Such a high concentration requires a membrane with minimum methanol crossover.

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http://dx.doi.org/10.1016/j.electacta.2017.02.097
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Numerous efforts have been made to modify Nafion-based membranes or fabricate new alternative membranes [15–17]. Among all of the alternative membranes, reinforced composite membranes appear to be the most promising solution [18–22] since they exhibit a high resistance against swelling and fuel crossover. Simultaneously, these composite membranes have been shown to have high longevity and chemical resistance, enhancing the performance of the device. One of the types of composite-based membranes involves a pore-filling concept that was first proposed by Yamaguchi et al. [23]. This concept was originally developed for liquid separation. Pore-filling electrolyte membranes are usually composed of two parts: a porous substrate and a filling electrolyte. The porous support matrix provides strong mechanical properties to suppress swelling and fuel crossover, while the electrolyte contains sulphonated polymers to provide proton conductivity. The choices of the substrate and electrolyte are both important and critical. The material of the porous substrate has a significant role as the membrane becomes swollen. Thus, it has to have a certain mechanical stiffness to restrict the highly swollen filled-electrolyte. Commercially available porous polyimide membranes were used in previous reports [12,28,30]. Additionally, polyvinylidene fluoride [29], polytetrafluoroethylene [31] and polyethylene [14] were also shown to be effective candidates in terms of their dimensional stability and fuel crossover. Meanwhile, the filling electrolyte is always the highly conductive component (of the pore-filling membranes), which is the main reason for water swelling. To obtain high proton conductivity, a high content of sulphonic acid groups (such as sulphonated polyethersulphone, sulphonated poly (styrene-ran-ethylene), poly (acrylic acid-co-vinyl), sulphonated copolyimide and Nafion) must be used as the filling component. Numerous combinations of materials have been used as the substrate and filling electrolyte to fabricate pore-filling proton exchange membranes (PFPEM) with high proton conductivity, longevity, low swelling and methanol crossover [32–34]. According to previous reports, sulphonated wholly aromatic (e.g., poly (aryl ether) derivatives) and vinyl monomers were the most commonly used filling electrolytes, while porous polyimide (PI) membranes were mostly used as the support matrix. The reasons for selecting these materials are that wholly aromatic polymers have strong mechanical properties, high chemical resistance and high thermal stability in the harsh fuel cell environment. As for the substrate, polyimide (PI) is chosen due to its mechanical stiffness and its effectiveness in suppressing swelling and methanol crossover. Additionally, after curing the PI-based substrates at a high temperature, a broad selection of the filling electrolyte solution can be introduced due to the insolubility of PI in most organic solvents.

Pore-filling composite materials have shown extraordinary dimensional stability (minimized swelling) and high resistance against methanol crossover when used in DMFCs [24–29]. Methanol crossover was highly suppressed due to the strong external stiffness of the polyimide (PI) substrate. It was found that under fully humidified conditions, free water swelling of these pore-filling membranes could be mechanically restricted and only the bound water of the sulphonic filling electrolyte would be present. This phenomenon suggests that this method should theoretically retain its conductivity while suppressing the dimensional change and at the same time minimizing fuel leakage. However, the conductivity of the previously reported pore-filling membranes is not large enough to compete with Nafion membranes.

To directly restrict the water swelling of an electrolyte with a high degree of sulphonation (DS), which provides high proton conductivity, epoxy resins have been introduced into the chemical structure of the electrolyte for the first time. In addition to limiting water swelling, this addition reduces fuel crossover due to its great chemical and mechanical resistance and strong network structure after solidification. The resulting synthetic electrolyte is found to be water soluble due to its high DS. A sulfonated polyethersulphone (PES) containing amino groups is used as the substrate to improve the conductivity and lower the contact angle of the substrate for the infiltration of the aqueous electrolyte solution. The amino groups of the PES substrate are used as a curing agent for epoxy. It is shown that the resulting composite membranes have higher conductivity and, at the same time, lower methanol permeation compared to a Nafion-based membrane. The results of tensile strain, thermogravimetric analysis (TGA), and Fenton tests reveal that the proposed composite membrane has even better mechanical and thermal properties as well as oxidative stability compared to Nafion. The single cell performance also shows a superior performance compared to Nafion in 10 M methanol.

2. Experimental

2.1. Material synthesis and preparation

Chemicals and reagents – Analytical grade (AR) hydroquinone (HQ) and 4,4-biphenol (BP) were purchased from Liaoning Pharmaceutical & Chemical Co., Ltd. and Honsyu Chemical Co., Ltd., respectively. Bis(4-chlorophenyl) sulphone (BCPS), epichlorchydrin, Tetra-n-butylammonium bromide, and 1-Ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) were all purchased from Aladdin Industrial Corporation. K_2CO_3 (Beijing Chemical Reagent, China) was ground into a fine powder and dried at 120 °C for 24 h before polymerization. Sodium hydroxide, ethanol and all of the other organic solvents were obtained from Beijing Chemical Works and used without further purification unless otherwise noted.

Preparation of amino-containing sulphonated poly (ether sulphone) (referred to as ASPES here) solution and membrane - The synthesis steps of ASPES are shown in Fig. 1, involving: 1) mixing BCPS (1.2634 g, 0.00886 mol), SBCPS (0.9137 g, 0.00186 mol), AP (0.1248 g, 0.00062 mol), BP (1.0391 g, 0.00558 mol), K_2CO_3 (1.0282 g, 0.00744 mol), sulpholane (8.0 mL) and toluene (4.0 mL) into a three-necked, round-bottomed flask equipped with a condenser, mechanical stirrer and a nitrogen inlet and outlet. The mixture was first stirred vigorously at room temperature (25 °C) for 30 min in nitrogen, and then, the system was heated to 150 °C and maintained at that temperature for reflux. After 4 hours, toluene and residual water were removed from the system and the temperature was elevated to 180 °C. The reaction was allowed to proceed for another 5 hours. After cooling to 60 °C, the mixture was poured into a container of deionized water. The product was pulverized into powder and washed with DI water four times followed by washing with ethanol the same number of times. Then, the resultant polymer was dried in a vacuum for 24 h and kept in a desiccator before use.

The porous ASPES membrane was fabricated based on the solution casting and evaporation method, as shown in Fig. 1. First, 10wt% of ASPES was dissolved by magnetic stirring for 12 h in N-Methyl-2-pyrrolidone (NMP) at room temperature in a sealed bottle to obtain a homogenous solution. Four separate samples of the prepared ASPES solution were mixed with $EMIMBF_4$ at concentrations of 50 wt%, 100 wt%, 150 wt% and 200 wt% of ASPES. The solutions (referred to as casting solutions) were continuously stirred for another 12 h to ensure uniform dispersion. The casting solutions were then filtered and slowly poured onto a flat glass substrate. The glass plates with casting solutions were held in an oven set at 60 °C for 24 h, after which the oven was put under vacuum where the plates remained for 48 h at 60 °C. After solvent evaporation, the membranes were removed from the glass

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