

Nafion–polyfurfuryl alcohol nanocomposite membranes for direct methanol fuel cells

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Abstract

Commercial Nafion 115 membranes were successfully modified by in situ acid-catalyzed polymerization of furfuryl alcohol (PFA) within Nafion structures. FT-IR and AFM were used to characterize the chemical and morphological structures of the Nafion–PFA nanocomposite membrane obtained. The methanol permeation experiments showed that the methanol flux through the Nafion–PFA nanocomposite membranes dropped by a factor of 2.2–2.7 when PFA loading was 3.9–8.0 wt.%. Importantly, the proton conductivity of the membranes decreased only slightly at a low PFA loading (<8 wt.%). The nanocomposite membranes with higher selectivity (e.g., proton conductivity/methanol crossover) achieved a much higher DMFC performance at both room temperature and 60 °C.

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1. Introduction

The direct methanol fuel cell (DMFC) is a promising device to replace existing batteries for a high energy density operation of portable electronic products. As a key part of a DMFC, a polymer electrolyte membrane is used between the anode and cathode to provide proton conductivity and to prevent internal electronic current between the two electrodes. Currently, perfluorosulfonic polymers such as Nafion are the most commonly used proton conductor for polymer electrolyte membrane (PEM) fuel cells because they have outstanding chemical, mechanical and thermal stability in addition to high proton conductivity. In DMFCs, however, high methanol crossover through Nafion membranes significantly lowers fuel efficiency and cell performance and thus impedes their commercial development [1]. In order to reduce methanol crossover, Nafion has been modified with a

variety of materials, yielding Nafion composite membranes. Ma et al. [2] and Choi et al. [3] reported that palladium and palladium-alloy deposited Nafion membranes were effective in reducing methanol crossover and giving a better cell performance at ambient temperature. Kim et al. [4] modified Nafion by a Pd impregnation method. The Pd–Nafion membranes showed a lower methanol permeability and maintained good proton conductivity. With this type of the nanocomposite membranes, a high concentration of methanol could be applied for DMFC without any power loss. Jung et al. [5] fabricated Nafion/montmorillonite nanocomposite membranes by direct melt intercalation of perfluorosulfonyl fluoride copolymer resin (Nafion resin) into the montmorillonite and modified montmorillonite. The methanol permeability of the composite membrane decreased slightly with increasing contents of montmorillonite. The composite membrane, however, improved the performance of the MEA only at high operation temperature (e.g., 125 °C). With the addition of molybdophosphoric acid and silica into Nafion, Dimitrova et al. [6] demonstrated an enhanced proton conductivity and lower methanol permeation through modified Nafion membranes. Tricoli et al. [7] dispersed two zeolites, chabazite and clinoptilolite into a

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Nafion matrix to form composite membranes. The results showed that the performance of chabazite–Nafion and of clinoptilolite–Nafion composite membranes was inferior to that of zeolite-free recast Nafion membranes with regard to both ion conductivity and methanol transport selectivity. Smit et al. [8] and Langsdorf and coworkers [9–11] studied the modification of Nafion by in situ polymerization of pyrrole. The polypyrrole modified Nafion membranes exhibited lower methanol permeation and proton conductivity, and enhanced cell performance. Shao et al. [12] prepared Nafion/polyvinyl alcohol composite membranes with a good selectivity of water over methanol and an enhanced cell performance as compared with commercial Nafion membranes. The strategy of forming so-called Nafion composite membranes by using an appropriate modifying material has proven to be effective for reducing methanol permeation and improving cell performance. The research still remains very active in pursuing a better proton conducting membrane for practical DMFC applications.

Very recently, we have reported a new approach to modify commercial membranes by in situ polymerization of polyfurfuryl alcohol (PFA) within the structures of Nafion [13]. Nafion–PFA nanocomposite membranes obtained exhibited largely reduced methanol permeation. It is anticipated that highly cross-linked, chemically stable PFA domains with a low swelling rate increase hydrophobicity and methanol resistivity of the nanocomposite membrane, and thus lower methanol permeation [14]. In addition, PFA is easily prepared by acid-catalyzed polymerization of its monomer (furfuryl alcohol, FA), and FA is miscible with mixtures of water and alcohols, and hydrophilic nature of the monomer allows uniform and thorough penetration into the hydrophilic structure of Nafion. In this paper, detailed characterization of the Nafion–PFA nanocomposite membranes and related cell performance of DMFCs will be presented.

2. Experimental

2.1. Membrane preparation

Commercial Nafion 115 membranes were cut into 2 cm × 2 cm pieces, and cleaned by following a literature protocol [15]. The membranes were boiled in 2% hydrogen peroxide for 1 h, rinsed with deionized water, followed by boiling in 0.5 M sulphuric acid for 1 h and washing thoroughly with deionized water. All cleaned membranes were stored in deionized water for later use. In order to uniformly incorporate furfuryl alcohol (FA, 98%, Lancaster), Nafion 115 membranes were converted into sodium form (Na–Nafion) by boiling in 0.5 M NaOH for 1 h, completely washing excessive NaOH away, and then drying at 80 °C for 30 min. The dried membranes were immersed in a solution of 6.2 g FA, 12.0 g isopropanol (98%, AJAX Chemical) and 12.0 g deionized water at room temperature for 24 h to ensure equilibrium

uptake of solution. The impregnated membranes were transferred into a 1.0 M sulfuric acid solution at room temperature for 2 min, and they subsequently were placed in an oven at 80 °C to initiate polymerization of the FA inside the Nafion membranes. A capped weighing bottle was used to weigh the dried membranes. The PFA content was determined by taking the ratio of the weight gain of Nafion–PFA membrane to the original Nafion 115 membrane. By repeating this procedure, the Nafion–PFA nanocomposite membranes with different loadings of PFA were obtained. The membranes were washed with ethanol, and boiled in a 1.0 M sulfuric acid solution to ensure complete polymerization and crosslinking of FA, and to convert Na–Nafion back to H–Nafion. The dark brown membranes were finally treated at 140 °C for 10 min, allowing for further microstructural rearrangements of the membranes [16,17]. The Nafion–PFA nanocomposite membranes containing different amount of PFA were denoted as N–XPFA (X stands for a weight percentage of PFA).

2.2. Characterization

The Nafion–PFA nanocomposite membrane and Nafion 115 membranes were characterized by a BioRad FTS165 FT-IR spectrometer (32 scans and at 2 cm⁻¹). The membrane samples were freeze-fractured in liquid N₂, and then dried under vacuum at room temperature for atomic force microscopy (AFM) studies. A Digital Instrument Nanoscope-IIIa atomic force microscope in tapping mode was used to image each sample in air at room temperature. The n-type silicon tapping mode AFM tip was mounted on a cantilever 3.9–4.3 mm thick, 32–33 mm wide with a force constant of 45–61 N/m (obtained from Fluoroware German). The resonance frequency was adjusted to be between 270 and 290 kHz with a sensitivity of 0.06–0.1 V/nm. All images were recorded in a 256 × 256 pixel format. To investigate the cross-sections on submicron scales, roughness was measured and compared in smaller areas using the Nanoscope IIIa roughness analysis software.

The proton conductivity of Nafion 115 membrane and Nafion–PFA nanocomposite membranes was obtained by measuring membrane impedance at room temperature [14,18,19]. The membrane was clamped between two compartments of an electrochemical cell filled with 5.0 M H₂SO₄ electrolyte solution. A planar Pt electrode parallel to the membrane was fixed in each of two compartments. The area of Pt electrodes was greater than 1.0 cm² of the membrane effective area to ensure accurate measurements. The impedance spectra were obtained on an AUTOLAB FRA2 impedance analyzer in the frequency range from 10 kHz and 100 Hz at ac signal amplitude of 10 mV and at room temperature. The proton conductivity was calculated by the equation

$$\sigma = \frac{l}{(R_{\text{cell}} - R'_{\text{cell}})S}$$

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