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Mordenite/Nafion and analcime/Nafion composite membranes prepared by spray method for improved direct methanol fuel cell performance

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ABSTRACT

The aim of this work was to improve proton exchange membranes (PEMs) used in direct methanol fuel cells (DMFCs). A membrane with a high proton conductivity and low methanol permeability was required. Zeolite filler in Nafion (NF matrix) composite membranes were prepared using two types of zeolite, mordenite (MOR) and analcime (ANA). Spray method was used to prepare the composite membranes, and properties of the membranes were investigated: mechanical properties, solubility, water and methanol uptake, ion-exchange capacity (IEC), proton conductivity, methanol permeability, and DMFC performance. It was found that MOR filler showed higher performance than ANA. The MOR/Nafion composite membrane gave better properties than ANA/Nafion composite membrane, including a higher proton conductivity and a methanol permeability that was 2–3 times lower. The highest DMFC performance (10.75 mW cm^{-2}) was obtained at 70 °C and with 2 M methanol, with a value 1.5 times higher than that of ANA/Nafion composite membrane and two times higher than that of commercial Nafion 117 (NF 117).

1. Introduction

Fuel cell technology has been developing rapidly because of a number of advantages that it possesses compared to conventional power sources, such as internal combustion engines or batteries. Fuel cells have higher energy efficiency than diesel or gas engines, and in using them, there is no pollution caused, as there is in burning fossil fuels, and no toxic by-product. Therefore, use of fuel cell can reduce greenhouse gases [1,2].

Direct methanol fuel cells (DMFCs) have been an attractive power source for portable electronics applications such as cellular phones, laptop computers, and personal digital assistants [3]. Methanol is used as a fuel source because of its high energy density, low cost, and the fact that it is easily handled and stored. DMFCs work at low and intermediate temperatures and are fed with a dilute solution of methanol [4].

Perfluorosulfonic acid membranes with a hydrophobic backbone and hydrophilic sulfonic acid side chain, such as Nafion, are currently used as proton exchange membranes. This is due to their high proton conductivity, chemical and thermal stability, and mechanical strength [5–8]. Nevertheless, DMFC has some severe problems. One of them is alcohol crossover through the membrane electrolyte resulting in waste of fuel, reduction of methanol-oxygen mixed potential at the cathode, and a serious decrease in fuel cell performance [1,7,9].

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In order to overcome these problems, a large number of methods have been developed to reduce methanol crossover in DMFC. Optimization has focused on operating parameters such as temperature [9], composition of the cathode feed [1,2,10], catalyst loading [3] and membrane thickness [11]. Many researchers have developed new composite membranes and modified the existing materials to alter their transport properties. The modification of Nafion has been studied by employing inorganic filler materials such silica, TiO_2, and zeolite.

Many researchers have selected inorganic materials to improve the water retention in the membrane and also to decrease the alcohol crossover [12–15]. Zeolite is a well-defined microporous structure of crystalline aluminosilicates containing silicon and oxygen in its framework. It has some characteristics that are suitable for DMFC. The regular porous structure of zeolite can also reduce alcohol permeation. In addition, the high surface acidity of zeolite provides a high proton conductivity.

Some examples of polymer-zeolite composite membranes for fuel cells are Nafion-Fe-silicate-1 membranes [16], Nafion-H-ZSM-5 membranes [14], Nafion-chabazite membranes [17], PVA-mordenite composite membranes [18], Nafion-mordenite hybrid membranes [19], sulfonated poly(ether ether ketone)/Analcime composite membrane [20], and Nafion/Analcime [21].

Among the various kinds of zeolite, mordenite (MOR) and analcime (ANA) have been great candidates for fabricating composite membranes. They are hydrophilic substances with molecular sieve properties [5,12], preferring to adsorb water to alcohol and providing a good proton pathway through the membrane while blocking the diffusion path of alcohol inside a Nafion composite membrane. In addition, mordenite and analcime are stable in acid and have high temperature tolerance. In our previous work, Yoonoo and coworkers [5] prepared Nafion/mordenite composite membrane to reduce methanol diffusion across the DMFC. The produced membranes exhibited reductions in methanol permeability of 21.62% and 4.27% at 30 °C and 70 °C, respectively, compared to a recast Nafion membrane. Kongkachuichay and coworkers [21] used Analcime and Faujasite as the zeolite in Nafion/zeolite composite membranes for PEMFCs. The proton conductivity of the Nafion/ANA composite membrane was enhanced 11 times at room temperature and 6.8 times at 80 °C, compared to Nafion membrane. It was reported that this enhancement might come from hydration inside the 3D channels of zeolite, with the hydrated water improving the proton motion or hydronium ion motion via the exchange of protons between hydronium ion and water molecules.

In this study, Nafion composite membranes with two fillers, mordenite and analcime, were fabricated by spray method. The properties of membranes with different fillers were studied and compared. The obtained composite membranes were characterized using SEM and mechanical test, and in term of solubility, water uptake, ion-exchange capacity (IEC), proton conductivity, methanol uptake, and methanol permeability. The DMFC performance test was also performed.

2. Experimental

2.1. Materials

Sodium aluminate (Al_2O_3 50–56%, Na_2O 40–45%), 3-mercaptopropyl triethoxysilane (MPTES) and hexamethylenimine (98.0%) were purchased from Sigma-Aldrich. Sodium silicate (neutral solution QP) was purchased from Panreac. Sodium hydroxide (97.0%), aluminumtrichloride (95.0%), and hydrogen peroxide (35 wt.%) were purchased from Ajax Finechem. A 20 wt.% Nafion solution was purchased from Ion Power. Sulfuric acid, ethanol, methanol, N, *N*-dimethylformamide, dichloromethane, ammonium cholride, toluene were purchased from ACI Labscan. De-ionized water was used throughout the study.

2.2. Methods

2.2.1. Synthesis of mordenite and analcime

Two types of zeolite were synthesized in this work: mordenite (MOR) and analcime (ANA). The corresponding synthesis procedures are described below;

2.2.1.1. MOR synthesis. The synthesis method was developed from the method of Corma and coworkers, using hexamethylenimine (HMI) as a template mixed with sodium silicate (Na_2SiO_3) as a silica source, sodium aluminate ($NaAlO_2$) as a alumina source, and sodium hydroxide (NaOH) as an alkali source [22]. The crystallization occurred in an autoclave operated hydrothermally and under agitation as follows. First, a mixture of 0.92 g $NaAlO_2$ and 0.60 g NaOH was dissolved in 124.2 ml of H_2O. Then, 7.61 g HMI and 25.639 g Na_2SiO_3 were added to the solution using vigorous stirring for 30 min. After that, the resulting gels were introduced into 60 ml of PTFE-lined stainless-steel autoclaves, rotated at 60 rpm, and heated at 170 °C for 24 h. After quenching the autoclaves in cold water, the solution was centrifuged. A portion of the solids was calcined in air at 580 K for 5 h to obtain MOR-Na.

2.2.1.2. ANA synthesis. The synthesis method was developed from that of Kim et al. using materials similar to the first method but without HMI as the template [23]. The crystallization occurred in an autoclave with hydrothermal system as follows: 4 g of water was mixed with 1.9 g of NaOH and stirred until the solid dissolved. Then, 1.43 g of $NaAlO_2$ was added into the solution and stirred until it too was dissolved. After that, 64.5 ml of water and 19.94 g of Na_2SiO_3 were added into the solution and stirred for 30 min. The resulting gels were introduced into PTFE-lined stainless-steel autoclaves and heated at 170 °C for 24 h. After quenching the autoclaves in cold water, the solution was filtered and washed until pH was less than 10 and dried at 100 °C to obtain ANA-Na.

2.2.2. Grinding of MOR and ANA

Grinding was used to reduce the particle size and obtain a homogeneous size of particles. The grinding procedure can be described in the following steps. First, 4 g of MOR (or ANA) and 10 ml of 0.5 mm zirconia ball grinding media were added into a container. Then, 15 ml distilled water was added to the container. Grinding speed was fixed by speed control. The sample was ground for 200 min to obtain a homogeneous distribution of particles of the smallest possible size.

2.2.3. Protonating of MOR and ANA

MOR and ANA surfaces were transformed into H^+ form in order to provide ionic paths for H^+ to travel from anode to cathode. To this end, MOR-Na and ANA-Na were treated to change Na^+ to H^+. The protonating method followed the procedure of Zanjanchi et al. [24]. The protonating procedure can be described as follows. First, 2 g of the MOR-Na (or ANA-Na) powder was stirred in 100 ml of 1 M NH_4Cl solution at room temperature for 24 h. At this stage, Na^+ was replaced by NH_4^+ and MOR-Na (or ANA-Na) became MOR-NH_4 (or ANA-NH_4) [25]. The suspension was subsequently vacuum filtered. Then, the sample was washed with deionized water and dried at 105 °C. MOR-NH_4 (or ANA-NH_4) was then calcined in a furnace at 550 °C for 5 h with a heating rate of 2 °C min^{-1}. At this point, NH_3 was released from NH_4^+ and left H^+ on the surface. In this stage, MOR-NH_4 was converted to MOR-H (ANA-NH_4 was converted to ANA-H).

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