



Surface modification of mordenite in Nafion composite membrane for direct ethanol fuel cell and its characterizations: Effect of types of silane coupling agent



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ABSTRACT

Mordenite (MOR) has been used to solve the alcohol crossover in direct ethanol fuel cells. However, the lack of compatibility has been a problem. This paper shows the compatibility improvement of MOR in a Nafion composite membrane for use in a fuel cell using four types of silane coupling agents: gamma-glycidoxypropyltrimethoxysilane (GMPTS), (3-mercaptopropyl)trimethoxysilane (MPTS), (3-mercaptopropyl)triethoxysilane (MPTES) and (3-mercaptopropyl)methyl-dimethoxysilane (MPDMS). The coupling agents were used to treat the MOR surface before mixing with Nafion. Each type of silane was treated carefully and differently, depending on its structure. Their characterizations were also described. The results showed that better compatibility and a noticeable reduction in ethanol permeability were achieved when using all silane-treated MOR in the composite. It was found that the Nafion/MOR-MPTES membrane had the highest proton conductivity at all temperature ranges from 30 to 70 °C. This was due to the fact that the sulfhydryl (–SH) functional group in MPTES provided the sulfonic group in its structure after the oxidation in the surface treatment process. These sulfonic groups at the MOR surface facilitated proton transport and improved the selectivity of the membrane.

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1. Introduction

At present, the use of hydrogen and methanol as fuels in the fuel cell is common and has been commercially applied widely. Direct ethanol fuel cells have been under focus due to low emission levels produced and low cost of fuel. Compared with methanol, ethanol has a higher energy density and specific energy [1,2]. Methanol is mainly obtained from petrochemical processes. Therefore, ethanol is considered a good choice for use in fuel cell development as it can be produced from renewable sources. The performance of a

fuel cell depends mainly on the type of catalysts and the membrane used. A significant problem with membranes in a fuel cell is the crossover of alcohol through the membrane from the anode to the cathode. Nafion is a common polymer membrane used as a proton exchange membrane in fuel cells, due to its high proton conductivity and good mechanical properties. The structure of Nafion consists of two parts: a hydrophilic part which is a sulfonic acid group, and a hydrophobic part which is polytetrafluoroethylene (PTFE) [3]. It has been found that the selectivity, proton conductivity and methanol permeability ratio of Nafion are higher compared to other polymers such as chitosan and SPEEK membranes. However, the main problem of Nafion as a membrane in direct alcohol fuel cells is the permeation of alcohol from the anode side to the cathode side, which is known as crossover. The permeated alcohol can react with O₂ and generate carbon dioxide at the cathode. As a result, the performance of the fuel cell is decreased [4]. In the report of Wang et al. [5], the selectivity values

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of chitosan and a Nafion[®] 117 membrane were 1.49×10^4 and 1.71×10^4 Ss/cm³, respectively. In the report of Maab and Nunes [6], the permeability of ethanol for Nafion 117 was 5 times higher than a plain SPEEK membrane. However, it was found that the power density of a fuel cell using a Nafion[®] 117 membrane was higher than that of a SPEEK membrane. It has been a good choice for selection as a matrix polymer for polymer exchange membrane fuel cells (PEMFC), especially if the ethanol crossover is improved.

Nafion polymer can be incorporated with filler, forming a composite membrane to improve its membrane properties [7–9]. Amiinu et al. [10] reported that doping Imidazole functionalized mesoporous silica into Nafion showed an increase in proton conductivity to 1.06×10^{-2} Scm⁻¹ at 130 °C. The presence of silica-imidazole within the matrix functioned as a transporting medium to facilitate proton conductivity. Kim et al. [11] enhanced the Nafion membrane by coating it with a delaminated AMH-3 (microporous layered silicate)/Nafion nanocomposite layer, which resulted in a low methanol permeability and maintained a high proton conductivity. The methanol permeability of the nanocomposite layer was 1.6 times lower than Nafion 115 due to the smaller opening pore size of the filler particles in the nanocomposite layer than methanol molecules. Thus, they played a role as a barrier and blocked the methanol molecules by a tortuous pathway effect. These results were consistent with Kumar and Kundu's work [12] that lower methanol permeability was achieved from Nafion coated and laminated with sulfonated polyvinylidene-fluoride (PVDF). Barbora et al. [13] studied neodymium oxide modified Nafion membrane for direct alcohol fuel cells. The pure Nafion and 5 wt.% composite membrane showed that the permeability of ethanol (1.22×10^{-7} cm²/s and 0.85×10^{-7} cm²/s, respectively) was less than that of methanol (1.38×10^{-7} cm²/s and 0.95×10^{-7} cm²/s, respectively) due to the larger molecule of ethanol. It was also found that the tensile strength of the composite membranes were higher than that of the pure recast Nafion membrane. Yen et al. [14] prepared sulfonated-silica/Nafion composite membranes, which have a higher selectivity than those of pristine Nafion. Adding silica-SH and silica-SO₃H to the membrane decreased the methanol permeability by approximately 30% and 15%, respectively. Another way to reduce alcohol crossover is by using a zeolite such as NaA-zeolite incorporated with Nafion which has been reported to successfully reduce alcohol crossover [15,16]. The study found that the methanol permeability of the Nafion composite membrane, incorporated with zeolite-NaA which was treated by APTS silane was up to 55.96% lower than that of a Nafion[®] 117 membrane. However, it was found that zeolite-NaA was not stable when used in a direct methanol fuel cell (DMFC) for long periods [17]. Various types of zeolite were incorporated with polymers, such as a zeolite beta-filled chitosan membrane. It was found that using zeolite beta can decrease the methanol permeability when compared with a pure chitosan membrane [5]. Devrim and Albostan [18] prepared the Nafion/zeolite composite membrane with different zeolite loading for a low humidity proton exchange membrane fuel cell (PEMFC). The results showed that water uptake and proton conductivity were enhanced due to the water retention properties of the zeolite and interaction between the Nafion and zeolite particles. PEMFC tests showed the 10 wt.% zeolite loading in the composite membrane was more stable and better than the Nafion membrane.

Cui et al. [19] synthesized Nafion-based membrane containing 5 wt.% and 10 wt.% of nano ammonium-X (NH₄-X) and submicron NH₄-X zeolite. The results showed that the water uptake, ion exchange capacity, and proton conductivity of the submicron 5 wt.% NH₄-X zeolite/Nafion composite membrane were higher than the Nafion membrane and the selectivity was more than twice of that of the Nafion membrane. The power density was 62.2 mW cm⁻² at 60 °C, which was 3 times higher than that of the Nafion membrane.

Moreover, the report of Kongkachuichay and Pimprom [20] showed that when incorporating analcime and faujasite as fillers with Nafion in PEMFC, the H₂ permeation of both types of Nafion/zeolite composite membranes was lower than that of the Nafion[®] 117 membrane. Nevertheless, mordenite (MOR) was suitable for use in a direct alcohol fuel cell [21]. MOR has 12-membered and 8-membered rings, resulting in 6.7×7.0 and 2.9×5.7 Å channels, respectively. The molecular size of water and ethanol is 2.6 Å [22] and 5.2 Å [23], respectively. Therefore, it can be seen that the ethanol molecule is smaller than the channels of the MOR. This can lead to better adsorption of water than ethanol. In summary, MOR as a type of zeolite has advantages of stability, high proton transport and higher water absorption than methanol or ethanol [24–26]. It can also be used in other applications [27]. It was found that there were some pinholes caused by poor compatibility between the Nafion polymer and the zeolite crystals which has been a problem reported in several studies [28–32]. Kwak et al. [33] synthesized MOR/Nafion composite membrane for high-temperature operation of PEMFC using various weight percentages of MOR. It was found that a higher MOR content led to lower tensile strength of the composite membranes (45 MPa for Nafion and 33 MPa for 5 wt.% MOR/Nafion). The strength was as low as 12 MPa for 20 wt.% MOR/Nafion membrane. This was due to poor compatibility between Nafion and MOR particles. The reduction in alcohol crossover and the higher compatibility can be achieved by improving the interfacial properties between the inorganic and organic parts in the composite membrane. In our previous work, Yoonoo et al. [21], 3-aminopropyl-triethoxysilane (APTS) and gamma-glycidoxypropyltrimethoxysilane (GMPTS) were used for MOR surface modification to increase the compatibility. It was found that GMPTS showed the best performance in DMFC, when 5 wt.% of ground and coarse (non-ground) MOR in Nafion were used. The proton conductivity of Nafion/MOR-GMPTS was slightly lower, but its methanol permeability was much lower than that of the recast Nafion membrane. Nafion/MOR-GMPTS also showed better performance in DMFC. The power density of the Nafion/MOR-GMPTS membrane was 1.11 times that of the recast Nafion membrane. A silane coupling agent was also used to modify zeolite surface for membranes used in gas separation [29,34]. Li et al. [29] reported that the permeability and selectivity of membranes made from silane modified zeolite were higher than those of membrane made from unmodified zeolite because the degree of partial pore blockage was decreased. Zhao et al. [35] reported the improvement of the adhesion strength of nanoparticles modified by grafting a silane coupling agent onto a TiO₂ nanoparticles surface. Wang et al. [36] used γ -mercaptopropyltrimethoxysilane with sulfhydryl (–SH) functional groups modified on the zeolite powders to improve the surface/channel of the zeolite substrates.

In this study, the focused was on reducing the permeation of ethanol and increasing the compatibility of the membrane that has been a crucial problem in DEFC. The main objective was the synthesis of Nafion/silanated-mordenite composite membranes to reduce ethanol permeability together with increasing the compatibility of the filler and the matrix for DEFC. MOR was used as inorganic filler and four types of silane were used as coupling agents to increase the compatibility. Further investigation of the effect of coupling agents in this study used gamma-glycidoxypropyltrimethoxysilane (GMPTS), (3-mercaptopropyl)trimethoxy silane (MPTS), (3-mercaptopropyl)triethoxysilane (MPTES) and (3-mercaptopropyl)methy-dimethoxysilane (MPDMS) to modify the surface of MOR before composite membrane fabrication. MPTS, MPTES, and MPDMS, which contain a sulfhydryl group that can convert to a sulfonic group, have not yet been used to improve the MOR surface, were used in this study to compare with GMPTS, as had been used in our previous studies [21]. These mercapto silanes should benefit from an increase in the sulfuric group (–SO₃).

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