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# Modified Nafion membranes for direct alcohol fuel cells: An overview

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A B S T R A C T

Direct alcohol fuel cells (DAFCs) have attracted considerable attention recently as alternative energy resources due to their high efficiency compared with other types of fuel cells. Currently, the two most common types of DAFCs are direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs), which use methanol and ethanol solutions as fuel, respectively. The most widely used polymer membrane for DAFCs is Nafion because it exhibits superior proton conductivity and excellent mechanical properties and chemical stability. However, Nafion membranes for DAFCs are expensive, have limited device lifetimes due to chemical and mechanical degradation, and have higher fuel crossovers through the membrane. Typically, to improve Nafion membranes, many researchers have modified Nafion membranes by modifying the Nafion matrix with organic or inorganic materials with different structures, sizes and compositions, modification techniques, or multilayered systems in order to improve the physical properties of Nafion. The characterization, properties, and performance of DAFCs from various types of modified Nafion membranes are critically reviewed by giving detailed examples. The challenges and future prospects for the modification of Nafion membranes for DAFC applications are also discussed.


**Contents**



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## 1. Introduction to direct alcohol fuel cells (DAFCs)

Direct alcohol fuel cells (DAFCs) can be defined as electrochemical devices that directly convert the chemical energy stored in liquid alcohol into electrical energy for transportation and portable applications [1]. DAFCs can be used as power sources for portable electric devices, such as cellular phones, notebook computers and others [2]. DAFCs have many advantages compared with proton exchange membrane fuel cells (PEMFCs), which use hydrogen as feed fuel, because DAFCs have relatively higher energy per mass densities, use low molecular weight alcohols, and are easier to handle, store and transport [3,4]. The alcohols that are used as fuel in DAFCs are methanol, ethanol, ethylene glycol and 2-propanol [5–8]. Besides, but there are also used 1-propanol [9] and glycerol [10]. However, methanol, ethanol, ethylene glycol and 2-propanol known as high energy densities, varying between 6.09, 8.00 and 8.58 kW h $kg^{-1}$ for methanol, ethanol and 2-propanol, respectively, compared with hydrocarbons and gasoline, which have energy densities of 10 and 11 kW h $kg^{-1}$, respectively [11].

Recently, two conventional types of DAFCs have attracted great attention among researchers: direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs), which use methanol and ethanol as fuel, respectively. Methanol can be considered as the most popular and widely used liquid alcohol fuel for DAFC applications because methanol is the simplest alcohol, containing only one carbon atom; it is cheap; and it is more efficiently oxidized than other alcohol fuels [12,13]. However, the use of methanol as a fuel has several disadvantages, including its relatively high toxicity, its high flammability and low boiling point (65 °C), and its tendency to pass through the fuel cell membrane from the anode side to the cathode side (i.e., its high crossover) [14,15]. The fuel crossover during DMFC operation results in a lower power output due to the chemical oxidation of methanol at the cathode with the help of the cathode catalyst [16]. These issues can limit the wide application of DMFCs.

Other alcohols such as ethanol can also be considered as alternative fuels. Ethanol has a higher energy density than methanol, it is non-toxic, and it can be easily produced from renewable energy sources [1,17]. In addition, USA and Brazil has a well-established supply chain of ethanol, and is currently available in most gas stations, which is not the case with methanol or other alcohols. In Brazil especially, ethanol is already distributed through the gas station network to the fuel thermal engine. Moreover, alcohol is an attractive fuel for the electric vehicle, since it can easily produce in great quantity by the fermentation sugar containing raw material from agriculture.

Song et al. [18] found that ethanol shows lower cross-over rates than methanol through Nafion membranes. They also found that ethanol has less negative effects on the cathode performance and exhibits slower electrochemical oxidation kinetics over a Pt/C cathode than methanol. However, ethanol contains two bonded carbon atoms, and this C-C bond is difficult to break with existing electrocatalysts at low temperatures [19]. As a result, the main product of the ethanol oxidation reaction (EOR) is acetic acid ($CH_3$–COOH) rather than $CO_2$ [20]. Therefore, alternative fuels to replace methanol and ethanol must be considered. Another choice of alcohols that can be used as an alternative fuel for DAFCs is ethylene glycol. Ethylene glycol has lower toxicity, safer handling, higher energy density, and a lower volatility due to a higher boiling point (b.p. = 198 °C) than methanol. In addition, ethylene glycol has a theoretical capacity 17% higher than that of methanol in terms of Ah $ml^{-1}$ (4.8 and 4, respectively), which is especially important for portable electronic applications [21].

The main hurdle for the success of DAFCs is still the lack of high performance catalysts and membranes. From the literature survey it is evident that much more work is focused on the development of different types of membrane. Many kinds of polymeric membranes were tested with direct methanol fuel cell (DMFC) since 1960 and they can now be testified for DEFC. The main objective is also how to achieve high proton conductivity with low fuel crossover through the membrane. Besides, the cost of Nafion has taken into account since it is affect the total cost for DAFC.

The polymer membrane used in DAFCs acts as a proton-conductive medium as well as a barrier to prevent direct contact between the liquid alcohol fuel and the oxidant. The research and development of novel proton-conductive membranes is one of the most challenging aims for improving the performance of DAFCs [7]. The polymer membrane should be able to reduce the fuel permeability while maintaining a high proton conductivity, as well as mechanical and chemical stability, to ensure the high performance of the DAFC [22]. Many studies have focused on either developing alternative membranes or modifying existing Nafion membranes to improve their alcohol barrier properties [23].

This paper presents a short review on the recent development of modified Nafion membranes for DAFC applications. An overview of the physicochemical and electrochemical properties of modified Nafion membranes is critically discussed. The performance of DAFCs using various types of modified Nafion membranes is summarized. Finally, the challenges and the future prospects of the development of modified Nafion membranes for DAFC applications are reviewed.

## 2. Nafion membranes

Over the past few years, Nafion has been the most commonly utilized polymer membrane in DAFC applications. Nafion is a perfluorinated polymer that consists of a polytetrafluoroethylene (PTFE) backbone and regularly spaced long perfluorovinyl ether pendant side chains terminated by sulfonic or carboxylic ionic functional groups. The hydrophobic polytetrafluoroethylene (PTFE) backbone of Nafion provides thermal and chemical stability, whereas the hydrophilic perfluorinated side chains act as proton-conductive groups [24,25]. The general chemical structure of a Nafion perfluorinated ionomer can be shown in Fig. 1, where X is either a sulfonic or carboxylic ionic functional group, and M is either a metal cation in the neutral form or an $H^+$ in the acid form [26].

Conventionally, Nafion, a perfluorosulfonyl fluoride copolymer from DuPont, is seen as the most suitable polymer membrane for DAFCs due to its high proton conductivity, excellent mechanical properties, good chemical stability, and commercial availability [27]. However, it has major disadvantages, such as high production cost, low conductivity at low humidity or high temperatures, loss of mechanical stability at high temperatures, elevated alcohol permeability and restricted operating temperatures [26]. The modification of Nafion by using polymer nanocomposite technology is the most common strategy to overcome the disadvantages