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Membranes for direct ethanol fuel cells: An overview

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HIGHLIGHTS

- DEFCs have emerged as alternative energy source.
- But many issue need to be addressed.
- This paper describes current problem and advancement of membrane in DEFC.

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ABSTRACT

Direct ethanol fuel cells (DEFCs) are attractive as a power source options because ethanol is a nontoxic, leading to ease of handling and a high energy density fuel, leading to high system energy density. However, to provide practical DEFCs power source there are several issues that still must be addressed including low power density, effect of ethanol crossover on efficiency of fuel utilization, electrical, mechanical and thermal stability and water uptake of the DEFCs electrolyte membrane. This paper describes the proton exchange membrane and alkaline exchange membrane for DEFCs, focusing on current problems and advancements in DEFC membranes. It also presents the specifications and performances of the membranes used in DEFC.

Contents

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1. Introduction

Much research and development are in progress to find alternative sources of energy for electricity which should be efficient, renewable and environmentally friendly [1–3]. However, challenges to their adoption still remain. Moreover, the increasing of portable devices consumption is essential for modern life, but their period of operation is limited due to energy storage limits [4,5].

Fuel Cells (FCs) are an alternative power source discovered by Sir William Robert Grove (an English lawyer turned scientist) in 1839 [3]. This power source is a candidate to replace the current battery and potential to achieve requirements for future sustainable power sources [6]. Peighambardoust et al. [7] described FCs as electrochemical devices that convert the chemical energy of a fuel (the reactant) such as methanol, ethanol or ethylene glycol into electrical energy without any fuel combustion. The energy is produced by the oxidation of the fuel into electricity, heat and waste products. FCs are system that are able to generate power with a higher energy conversion efficiency and more environmental friendly than other systems [5,7]. The classification of FCs depends on several parameters, such as the operating temperature and pressure conditions, fuel cell structure, membrane type, electrolyte type, exchanged ion, and reactant type. Generally, conventional classifications are made according to the electrolyte used in the fuel cells [7].

Proton exchange membrane fuel cells (PEMFCs) and alkaline fuel cells (AFCs) are convenient for portable device applications due to their low working temperature, non-corrosiveness and functional flexibility in any orientation. The prototypical fuel for PEMFCs and AFCs is hydrogen (H_2), because it is the most electrochemically active fuel regarding its rate to ionize at low voltage loss (over potential) during reactions [8]. The oxidation of H_2 produces clean energy with limited carbon dioxide (CO_2) emissions, which leads to a low environmental impact. However, the disadvantages of hydrogen include that it's not a primary fuel and not a naturally existing gaseous fuel. Thereby it's requiring an external reforming process. It is also difficult to store the fuel, necessitating bulkier and heavier systems with increased production costs [9–14]. Alcohols are another fuel that has been widely applied in ambient conditions for FCs [15]. Direct alcohol fuel cells (DAFCs) have a number of attractive properties. Alcohols are liquids at ambient conditions making them easy to handle, store and transport. Moreover, because alcohols are liquid, they also have higher volumetric energy density than H_2 fuel at room temperature and pressure. In addition, some alcohols are renewable and have low toxicity [13,14,16,17]. Therefore, DAFCs are more compact without the need for a heavy and bulky external fuel reformer [10,16,17]. As preliminary DAFCs, direct methanol fuel cells (DMFCs) are a common alcohol fuel cell that has been widely investigated due to its high current density 6.09 kW h kg^{-1} [18], not requiring electricity to recharge [1,3], adaptability to a quick refueling system [3,19], low emission of pollutants [2,19], longer cell lifetime due to superior specific energy density [1], inexpensive fuel and ease of transportation and storage. Furthermore, methanol has high energy conversion efficiency [2,5,18]. Unfortunately, DMFCs have several technical problems as methanol is volatile and toxic [13,18]; requires expensive platinum (Pt)-based catalysts [18]; exhibits high methanol cross-over through the polymeric Nafion® membrane, which effects current production and decreases cathode efficiency [10,20]; and is non-renewable [21].

Ethanol is an attractive alcohol that is suitable for direct oxidation FCs. Ethanol has a variety of advantages over other fuels, such as hydrogen and methanol, including a substantially higher energy density of 8.00 kW h kg^{-1} and nontoxic, which avoids environmental pollution issues [22–28]. Song et al. [29] reported that the performance of ethanol in direct oxidation FCs is better than that of methanol due to the lower crossover rate of the fuel, which decreases the effect on cathode performance.

Moreover, ethanol is sustainable due to its natural availability [21,27] and is also classified as a renewable energy because it can be produced in bulk from agricultural bio-processes via a fermentation process of biomass from agriculture, forestry and urban residues [9,21,28,30]. Ethanol is a sustainable fuel, simple to handle, store, and transport and supports fast refueling [22–26,29,31,32]. In this sense, DEFCs have emerged as an excellent alternative power source for portable device due to their high energy density (energy per unit volume), non-toxicity and availability of ethanol [21,33]. Badwal et al. [34] presented a comprehensive review on DEFCs including the source and production of ethanol, performance and market application as well as the commercial status of ethanol based FCs technology for transport and stationary application. Two types of DEFCs have been recognized: direct ethanol-proton exchange membrane fuel cells (DE-PEMFCs) were the first type of DEFCs studied [9,34,35] and alkaline anion exchange membrane-direct ethanol fuel cells (alkaline AEM-DEFCs) [34,36,37]. Fig. 1 presents the basic schematic diagram and operation process of DE-PEMFCs and alkaline AEM-DEFCs.

Hence, the research and development of component in DEFCs especially electrolyte membranes are critical issue in deploying DEFCs as a feasible and economically practical energy source. The electrolyte membranes, as the "heart of the DEFCs" having the essential function to separate the chemical reaction at the anode from that at the cathode, fuel barrier to protect the reaction between fuel and oxidant and tend to allow protons move freely [38,39]. The primary requirement of electrolyte membranes for applied in DEFCs are following the: low ethanol permeability, high proton or ionic conductivity (must be exceed ($\geqslant 100 \times 10^{-3}$ S cm^{-1}) to provide a large current with minimal resistive losses and electrons isolation. In additions, the material of electrolyte membranes must be low cost production, ready availability, film forming ability as thin as possible (50–80 μm), good mechanical stability, long-term chemical and thermal stability and water management. Furthermore, the extra characteristic of materials to provide electrolyte membranes must be made of biodegradable, nonhazardous and environmentally benign [27,38–41].

Apparently, perfluorinated sulfonic acid electrolyte membrane (Nafion® membrane, manufactured by DuPont) is commonly used in PEMFCs due to excellent chemical and electrochemical properties as well as the mechanical stabilities with high proton conductivity. Unfortunately, the drawback of Nafion® membrane is due to high cost production and high permeability fuels inside the membranes which lead to the swelling problem and cause the loss of fuel. As a result, the performance of PEMFC decreases. One of the main reasons of the drawback is performance drop of the membrane at elevated temperature above 80 °C. This is due to the dehydration of the membrane give adverse effects in their proton conductivity and mechanical stability. Therefore, considerable efforts to improve or finding an alternative membrane for FCs application are the key requirement [42–45].

Due to the short coming of Nafion® membrane in acidic media, anion exchange membrane (AEM) is introduces as an electrolyte membrane in alkaline FCs. This membrane provides several advantages like reduction of fuel crossover from anode to cathode and reduces the fuel loss. Moreover, alkaline media was proved to improve the water management [46–50]. However, there are challenges for the AEM consumption such as the high of OH^- conductivity are highly desired for obtaining a higher power density and the availability of suitable ionic conductivity as well as chemical stability under alkaline FCs operating conditions. For example, the quaternized co-monomers are usually used as the charge carrier [46,47]. Therefore, this study will present the current development of electrolyte membrane for DEFC, including those of DE-PEMFCs and