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Approaches to overcome the barrier issues of passive direct methanol fuel cell – Review



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ABSTRACT

Direct methanol fuel cells (DMFCs) within all types of fuel cells are the most viable alternative to lithium-ion batteries in the portable application, and recently attracted much attention. This review provides a comprehensive overview of the passive DMFC barriers viz. methanol crossover, slow kinetics, water management, heat management, species management, durability and stability and cost for commercialization. Furthermore, it focuses on different approaches to overcome discussed barriers of passive DMFC. It is shown that the critical challenge regarding to minimize methanol crossover through the membrane using various hybrid membranes and methanol transport barrier so that the cell performance can be maximized. Regarding to reduce the catalyst cost with better kinetics, it is expected for developing non noble catalyst for passive DMFC. The challenges related to the operating temperature of passive DMFC is the selection methanol concentration, current density, ambient temperature, air humidity, cell orientation, membrane thickness, cell design, etc. which affects the cell performance. The several methods related to the water management layer deals with transport of the water produced on the cathode to the anode through the membrane and the cathode with minimum water flooding.

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1. Introduction

The power consumption for personal portable electronic devices has been increased day by day with development, and it is expected more in the future. The conventional batteries are insufficient to handle the portable electronic device. Thus, looking for the alternative energy sources for mobile devices, the fuel cell is found to be the best suitable choice. The fuel cell produces the electricity as long as fuel is supplied, which is the basic difference between the battery and fuel cell. The polymer electrolyte membrane fuel cell (PEMFC) is the most attracted fuel cell due to the flexibility of using solid electrolyte and avoided electrolyte leakage problems. H₂ gas and liquid alcohol are the fuel choices in PEMFC for portable application. PEMFC uses methanol, ethanol, 1-propanol, 2-propanol and ethylene glycol as the liquid fuel. Some alcohol has a very good energy density as shown in the Table 1, which is close to gasoline and other hydrocarbon [1]. The energy density (W_e) or specific energy is a stored energy in fuel per unit mass is given by the expression, W_e (kWh kg⁻¹)= $\Delta G^{\circ}/3600$ M.

Where, M is the molecular weight of fuel.

Methanol is the best fuel choice for portable application within all types of liquid fuel PEMFC called as direct methanol fuel cell (DMFC). The electro-oxidation of methanol in DMFC produces the electrons; hence conduct electricity in a complete circuit. All the reaction in DMFC occurs in the membrane electrode assembly (MEA). The MEA consists of an electrolyte membrane sandwiched in between the anode and cathode together. The produced electron from the reaction moves from the anode to the cathode side. Fig. 1 shows the reaction flow chart of a passive DMFC. The methanol solution is fed into the anode side diffuses through a diffusion layer. Methanol is oxidized to ${\rm CO}_2$ at the anode that allows six protons travel through polymer electrolyte and allows six electron travel through the external circuit to produce electricity. At the same time, ambient air diffuses through a diffusion layer is reduced to water at the cathode side. Hence the complete electrooxidation of methanol generates electrons, protons, CO2 and heat as follows.

Anode reaction:

$$CH_{3}OH \, + \, H_{2}O \, \rightarrow \, CO_{2} \, + \, 6H^{+} \, + \, 6e^{-} \quad \, \Delta H \, = \, 130 \cdot 72 \; kJ/mol \; (1)$$

Cathode Reaction:

$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$
 $\Delta H = -857 \cdot 49 \text{ kJ/mol} (2)$

Overall reaction:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$$
 $\Delta H = -726 \cdot 77 \text{ kJ/mol} (3)$

The advantages of DMFCs over the other types of fuel cells are; smaller size, light in weight, low working temperature, high-energy density and easy fuel storage [2,3]. It is convenient and less

Table 1 Thermodynamic data of alcohol [1].

Fuel	ΔG° (KJ/Mol)	E _{cell} (V)	W _e (kWh/kg)
CH_3OH C_2H_2OH C_3H_3OH Gasoline	-702 -1325 -1853	1.213 1.145 1.067	6.09 8.00 8.58 10.5

 $[\]Delta G^{\circ}$ – Gibbs energy: total energy to create a system and make room for it minus the energy provided by environment.

W_e – Energy density: specific energy stored in fuel per unit mass.

expensive to carry smaller containers of methanol than to carry heavy batteries.

The DMFCs are classified into two categories such as passive and active DMFCs. In the passive DMFC, the reactants (methanol and oxygen) are supplied up to the catalyst layer as well as the products (CO₂ and water) are removed out of the cell by passive means, i.e. diffusion, natural convection and capillary action, etc. In active DMFC the fuel and oxygen are supplied by external agencies such as pump, blower, etc. Compared to active DMFCs, the passive DMFCs are compact, simple in construction and have low parasitic power losses [3-5]. Thus, passive DMFC is a good option for conventional battery replacement for portable application because of no auxiliary element [2]. High energy for a longer time, reduction in size and immediate recharging would make passive DMFC most promising energy resources to commercialize [5]. However, passive DMFCs have some barrier issues for commercialization such as methanol crossover (MCO), the slow kinetic reaction of methanol, heat management, water management, durability, stability and cost etc.

The purpose of this review work is to discuss and conclude the critical challenges which diminish the commercialization of passive DMFC. The paper also summerizes the past research effort and future direction towards the discussed problems followed by approaches with examples. Emphasis is focused on elaborating the various approches such as material development of membrane, catalyst, catalyst support, gas diffusion layer, microporous layer, current collector and different transport barrier followed by cost, design structure, operating condition, operating orientation and operating duration. The paper also provide an outlook for future research directions. The remainder of the review is organized as follows: Section 2 discusses the basic structure of passive DMFC; Section 3 discusses the critical challenges of passive DMFC. This section also provides the possible approaches to diminish the challenges of passive DMFC and finally a concluding remark is given in the Section 4.

2. Passive DMFC single cell

Fig. 2 shows passive DMFC single cell structure and components [6]. The sequential component of passive DMFC is anode end plate, anode reservoir, anode current plate, MEA, cathode current collector plate, and cathode end plate. The gaskets are placed in between each component to avoid the methanol leakage and nut and bolt are required to assemble all components. The main important components in DMFC are proton exchange membrane, anode-cathode catalyst, and current collector plate as they really

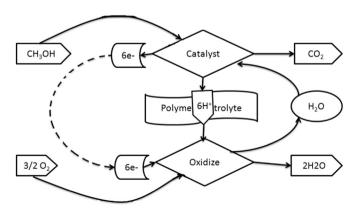


Fig. 1. Reaction Flow chart of Passive DMFC.

 E_{cell} – Electromotive force (emf): the potential of the system to perform electrical work measured by voltage.

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