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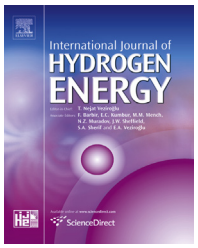

High-performance direct methanol fuel cell with optimized membrane electrode assembly: A theoretical approach

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ABSTRACT

Methanol/water crossover through proton-exchange membranes and low cell voltage resulting from sluggish catalytic reactions are major issues that must be overcome to commercialize direct methanol fuel cells (DMFCs). Three key performance indices (low methanol crossover rate (MCO), low water–transfer coefficient, and high cell voltage) can be improved by optimizing the design of the DMFC membrane electrode assembly for the cell operating conditions. Using computational techniques with a one-dimensional DMFC model, the present study proposes guidelines for constructing a high-performance DMFC with a focus on membrane electrode assembly (MEA). First, the membrane thickness is determined by balancing the MCO and ionic conductivity for both the fluorocarbon (FC) membrane and the hydrocarbon (HC) membrane. Second, the material composition of the cathode catalyst layer (cCL) is optimized by balancing charge transfer and mass transfer. Finally, the anode diffusion layer (aDL) is optimized according to the cell operating conditions. Compared to the referenced baseline cell, this optimization process is predicted to improve the cell voltage by 19% and decrease methanol crossover by 64%.

Introduction

Direct methanol fuel cells (DMFCs) are electrochemical power generators that produce electricity via a methanol oxidation reaction (MOR) in the anode and an oxygen reduction reaction (ORR) in the cathode, as summarized in Eq. (1).

$$\begin{array}{l} CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (\text{anode}) \\ 6H^+ + 6e^- + (3/2)O_2 \rightarrow 3H_2O \quad (\text{cathode}) \\ \hline CH_3OH + (3/2)O_2 \rightarrow 2H_2O + CO_2 \quad (\text{overall}) \end{array} \tag{1}$$

DMFCs have strong potential applications as mobile or automotive power sources because of their high theoretical energy density (~4800 Wh l^{-1}) [1]. Another advantage of DMFCs is that their fuel mixture of water and methanol is inexpensive and widely available. However, DMFCs are unlikely to become widely available on the market despite the substantial efforts of engineers and scientists to commercialize them. The first reason for the delayed commercialization of DMFCs is the popularity and competitiveness of Li-ion batteries. The other reason relates to technical issues regarding DMFC, which are listed in Table 1. Among these technical issues, three key problems remain unresolved: i) low energy conversion efficiency because of sluggish catalytic reactions, ii) methanol crossover from anode to cathode through the proton-exchange membrane, and iii) water loss from the anode. To improve DMFC performance, various techniques have been proposed. For example, by feeding methanol vapor instead of a

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Table 1 – Problems to overcome for DMFC commercialization [2].

Category	Problems	Consequences
Anode catalyst	methanol oxidation kinetics	Requires high catalyst loading
	catalyst poisoning	Reduces DMFC lifetime
Cathode catalyst	oxygen reduction kinetics	Requires high of catalyst loading
	catalyst poisoning	Reduces DMFC lifetime
Membrane	methanol crossover	Degrades cell performance and fuel efficiency
	low ionic conductivity	Degrades cell performance
Water management	low concentration fuel	Lowers DMFC energy density
	large water crossover	Not sustainable for steady operation
Fuel management	low flow rate required	Not sustainable for steady operation
Gas management (anode)	CO_2 removal	Causes strong two-phase flow, large anode stoichiometry, and voltage fluctuation
Gas management (cathode)	air supply	Requires pumping power, and the mechanism becomes complex and bulky

liquid fuel mixture, the system's energy density was improved; however, this technique requires an additional heating source to vaporize the liquid fuel [3]. Additionally, the insertion of a micro-porous layer (MPL) between the catalyst and diffusion layers effectively mitigated methanol and water crossover in several studies [4–6]. Indeed, anode MPLs have been reported to play an important role in controlling methanol crossover, whereas cathode MPLs effectively reduce water loss by building hydraulic pressure between the membrane and the cathode catalyst layer (cCL). A nonuniform distribution of fuel supply in the anode eventually causes large overpotential and severe methanol crossover, thus degrading cell performance. Jung and Wang [7] proposed a streamlined graded structure for DMFCs to improve cell performance by mitigating the nonuniform distribution of fuel concentration in the anode. Their concept aimed to control the mass-transfer resistance along the flow channel direction by changing the channel shape and porosity of the diffusion layer. By converting the diffusion-dominant structure to a convection-dominant structure, anode nonuniformity was significantly improved under ultra-low flow stoichiometry conditions [8].

The membrane electrode assembly (MEA) is a key component of a DMFC in which several, complex transport phenomena occur simultaneously. Typically, MEAs have a sandwich structure consisting of five layers; the anode diffusion layer (aDL), anode catalyst layer (aCL), membrane, the cathode catalyst layer (cCL), and cathode diffusion layer (cDL). When an MPL is inserted between the catalyst and diffusion layers, the MEA contains seven layers, as depicted in the model geometry (Fig. 1).

Since multiple chemical species react together as multiphases, the physico-chemical phenomena occurring in DMFCs are very complex. Hence, substantial effort has been devoted to theoretically and computationally construct DMFC models and use the models to elucidate physical phenomena. DMFC models can be categorized as one-dimensional, two-dimensional, and three-dimensional models according to the model's dimension. Typically, one-dimensional models are mathematically analytical and are strictly driven by simplified governing equations.

One-dimensional models have the advantage of rapid calculation, enabling engineers to conduct many quick parametric studies to determine guidelines for the design of a new DFMC. Meyers and Bennett [9] proposed a one-dimensional analytical model of DMFC anodes to study the effects of material properties on DMFCs' fuel efficiency. By incorporating electrochemical kinetics, they further extended their analytical model to predict DMFC performance quickly, according to the properties of materials used [10]. However, their model did not consider two-phase flow characteristics in DMFCs. Based on experimental observations, Kulikovsky [11] reported a simple one-dimensional DMFC model focusing on the effect of bubble evolution in DMFCs on cell performance.

Since conventional DMFCs have flow-field structures, through which liquid fuel and air are supplied, they are essentially multi-dimensional devices in which several multiphase and multi-dimensional physical phenomena occur. In particular, large-format DMFCs may suffer from severe nonuniformity of their fuel supply and experience significant voltage loss and fuel crossover because of the dimensional effects [7]. Therefore, designing and analyzing the flow-field structures of DMFCs to uniformly supply fuel and oxidizer to the electrodes are important activities. For these purposes, engineers can utilize multi-dimensional DMFC models. Various relevant modeling approaches have been introduced by several research groups. Kulikovsky [12–14] theoretically studies the dimensional effect on DMFC performance using a two-dimensional DMFC model. Wang and Wang [15] introduced a two-dimensional DMFC model considering both liquid- and gas-phase flows by applying computational fluid dynamics techniques. Yang and Zhao [16] applied the classical multi-phase flow model to their two-dimensional DMFC model and then further improved the two-dimensional model by integrating non-equilibrium evaporation and condensation effects [17] and extending the ability to capture the dynamic response of cell voltage to sudden changes in fuel concentration, oxygen concentration, and current load [18].

Three-dimensional models facilitate investigating the more complex physical phenomena that occurs in three-dimension, such as two-phase flow and non-isothermal effects in DMFCs. Typically, three-dimensional simulations are conducted in steady-state mode because transient simulations require very long computational times and high costs. Yang et al. [19] extended their two-dimensional model to three-dimensions to study flow-channel directional phenomena in DMFCs. By applying computational fluid dynamics techniques, Liu and Wang [20] developed a three-dimensional