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Heat and Mass Transfer Characteristics of Direct Methanol Fuel Cell: Experiments and Model

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Abstract

A three dimensional non-isothermal model is developed for anode side of Direct Methanol Fuel Cell (DMFC) to study the heat and mass transfer characteristics on cell performance. Electrochemical reaction is coupled with cell current density by Tafel kinetic expression. Commercial software "Fluent 6.3"is used for computation. Methanol and temperature distribution in the anode side are predicted. Double channel flow field is used to investigate the methanol distribution and its effect on cell performance. Methanol and water crossovers in the cell are the major controlling parameters which control the cell performance. The model is also used to predict the methanol crossover effect on Fuel Utilisation Efficiency (FUE) and cell performance. The cell efficiency increases from 7 to 13% with decreasing methanol concentration of 1 to 0.25 M. Net water transfer coefficient is high at low current density and decreases with increasing current density. Experiments were conducted with varying cell voltage and the model results are compared with experimental data.

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Keywords: DMFC; Methanol crossover; water transfer; mixed potential; Fuel utilization efficiency

1. Introduction

In recent years, DMFC is becoming a competing energy conversion device due to its simple structure, environmental friendly, easy handling of fuel and high energy density. It is an energy conversion device which converts chemical energy of fuel in to electrical energy. The major challenging issue to commercialize of DMFC is methanol and water crossover. Xu et al. [1] used water management layer to reduce water crossover. Methanol and water crossover rate were measured experimentally. It is found that the water crossover is constant with increasing methanol concentration and the cell performance reduces due to mass transport limitation of oxygen. The cell

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without water management layer gives better performance. Xu and Faghri [2] developed a two dimensional model to study the water transfer characteristics in passive DMFC. Water transfers from cathode to anode when increasing humidity of air. This enhances liquid saturation at the cathode which reduces water crossover from anode to cathode. The water crossover flux increases with increase in cell current density and methanol concentration.

Nomenclature

$C_{ch}^{ac/m}$	Methanol concentration in ACL and membrane interface mol/m^3
$D_w^{eff,m}$	Effective diffusion coefficient of water in membrane m^2/s
F	Faradey's constant C/mol
i_{cell}	Cell current density A/m^2
N_{ch}^m	Methanol flux in membrane mol/m^{2}s
N_w^m	Water flux in membrane mol/m^{2}s
N_w	Total water flux in membrane mol/m^{2}s
n_d	Electro-osmatic drag coefficient of water
t_d	Diffusion layer thickness m
ε	porosity
α	Water transfer coefficient
λ	Electro-osmatic drag coefficient of methanol

Olivera et al. [3] developed a one dimensional model to study the heat and mass transfer processes in DMFC. The model is used to predict the temperature profile, methanol crossover and water crossover from anode to cathode. Ge and Liu [4] developed a three dimensional model of DMFC. The effect of porosities of diffusion and catalyst layers, the effect of methanol flow rate and the effect of channel shoulder width on methanol crossover and cell performance are presented. Li et al. [5] developed a two dimensional, two phase model to study the mass transport processes of methanol and water through the membrane. Anode microporous layer is used to reduce methanol and water crossover and it plays a significant impact on reducing methanol crossover. In this work, a full cell model is developed for anode side of DMFC. The model is used to predict methanol, temperature distribution and the effect of methanol and water crossover on cell performance.

2. Three dimensional model

The model domain consists of anode channel (ACH), anode diffusion layer (ADL), anode catalyst layer (ACL) and membrane (MEM). The dimension of model domain is given in Table 1. The Flow field used in this study is shown in Fig.1. Mass, momentum and energy conservation equations coupled with electrochemical reaction rate equations are solved by Fluent 6.3. Diffusion coefficient of species and source terms are incorporated in the model using User Defined Functions (UDF). For a given cell current density, anode potential is computed depending on the methanol concentration. This procedure is repeated for different cell current density. The cell voltage is estimated and the polarization curve is obtained.

Table 1. Dimension of DMFC model domain.

Description	Dimensions
Active area of the cell (mm)	50X50
Diffusion layer thickness(mm)	0.14
Catalyst layer thickness(mm)	0.03
Membrane thickness(mm)	0.18
Chanel width, depth and rib width (mm)	1

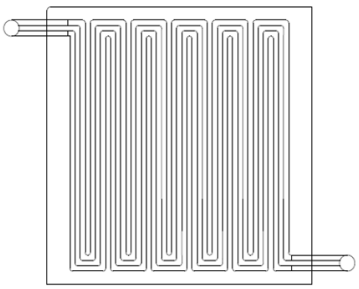

Fig.1 Double channel serpentine flow field

2.1. Boundary conditions

i. Anode side of DMFC is considered for analysis to reduce computation time.
ii. Methanol velocity is given at the anode channel inlet. Mass fraction of reactants is given as input.
iii. Ambient pressure is given at the channel outlet.
iv. Methanol crosses through the membrane is completely oxidised and converted to CO_2. Methanol flux at the cathode catalyst layer is zero and the cell temperature is maintained at 60°C.

Reactant properties, source terms and other parameters are found in elsewhere [3-5]. Methanol transfer through the membrane is given by,

$$N_{ch}{}^{m} = \frac{\lambda_{ch}\, i_{cell}}{F} + \frac{\varepsilon D^{m}{}_{ch}\, C_{ch}{}^{ac/m}}{t_d} \tag{1}$$

Water transfer through the membrane is given by

$$N_w{}^{m} = -D_w{}^{eff,m}\left[\frac{dC}{dx}\right] + n_d \frac{i_{cell}}{F} \tag{2}$$

Water produced in cathode is due to water transfer through the membrane ($N_w{}^{m}$), water generation due to methanol crossover ($N_{mco}{}^{w}$) and water generation from oxygen reduction at the cathode ($N_o{}^{w}$). Net water flux produced is given by,

$$N_w = N_m{}^{w} + N_{mco}{}^{w} + No^{w} \tag{3}$$

$$N_w = N_m{}^{w} + 2N_{ch}{}^{m} + \left[\frac{i_{cell}}{2F}\right] \tag{4}$$

The net water transfer coefficient is expressed by,

$$N_w = \left(\frac{i_{cell}}{6F}\right)(\alpha + 1) \tag{5}$$

3. Experimental setup

A commercial Membrane Electrode Assembly (MEA) area of 25cm^2 is used for experiments. Catalyst loading of 4mg/cm^2 Pt/Ru is used in anode and that of 4mg/cm^2 Pt in cathode. Double channel serpentine flow field is used in graphite plate (both anode and cathode). Methanol is supplied at 14ml/min and air is supplied at 600ml/min. The graphite plate temperature is controlled by temperature controller and is considered as cell temperature. Electronic load bank is used to measure cell voltage and current.

4. Results and Discussion

The model results are obtained at a methanol flow rate of 14ml/min. The cell performance is predicted for different current with varying cell voltage and the cell temperature is at 60 °C. Methanol and water from anode channel diffuses through the diffusion layer to catalyst layer. Methanol and water transfer process through the membrane is studied with varying methanol concentration and cell current density.

4.1. Model comparison

Fig.2 shows the model comparison with experimental data. The model results agree with experimental data at 0.5M and no much diference at 0.25 M and 30% at 1 M. This may be due to the assumption of porosity and permeability of diffusion and catalyst layers, exchange current density and charge transfer coefficient.

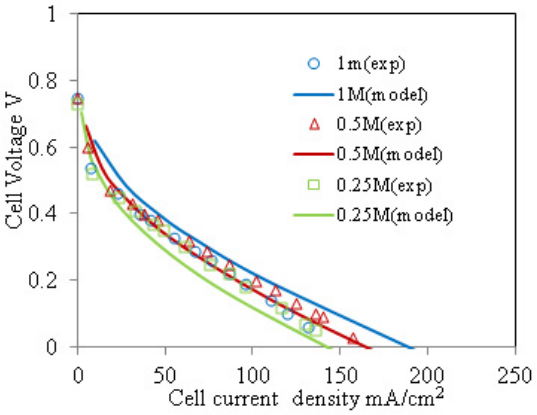

Fig. 2 Model comparison with experimental data

4.2. Methanol distribution in anode catalyst layer and membrane interface

From Fig.3a, it is seen that the channel area exposed to MEA have high mass fraction of methanol. Depending on the applied current density and feed concentration, methanol concentration in the anode catalyst layer varies. Mass fraction of methanol indicates the cell current density distribution. At low current density, methanol reaching the membrane is more compared to high current density. This is due to low consumption rate during electrochemical reaction and high diffusion rate of methanol and leads to high methanol crossover rate at low current density. Methanol diffuses through the membrane and oxidizes with oxygen at the cathode catalyst layer. This affects the cell performance due to mixed potential. Methanol diffusion is due to concentration gradient and electro-osmotic drag. It is seen that the mass fraction of methanol under the channel region is high. At the corner of even numbered channel, methanol diffusion is high. Double channel serpentine takes a turn and has long channel length which helps in methanol diffusion under the rib. Methanol distribution in anode catalyst layer controls the cell performance which can be controlled by flow field design and operating conditions such as cell temperature and methanol concentration. Effect of methanol concentration on power density is shown in Fig.3b. Cell current density increases with increase in methanol concentration and depends on methanol availability at the anode catalyst layer. The peak power density also increases with increase in concentration.

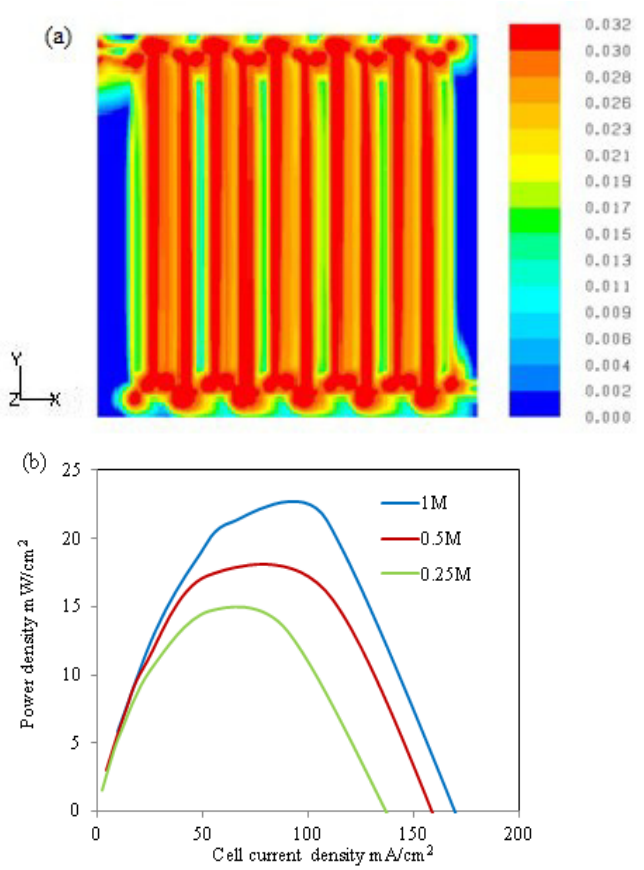

Fig. 3 (a) Methanol distribution (mass fraction) in anode catalyst layer and membrane interface (b) Effect of methanol concentration on power density

4.3. Temperature distribution in anode channel

From Fig.4, it is seen that the graphite plate temperature is maintained at 60 °C and the methanol is sent at 27 °C. The methanol solution temperature is raised to 57 °C when it passes through the flow field plate. The methanol solution at high temperature is sent to the methanol tank and circulated back to the fuel cell. This helps in improving the cell performance.

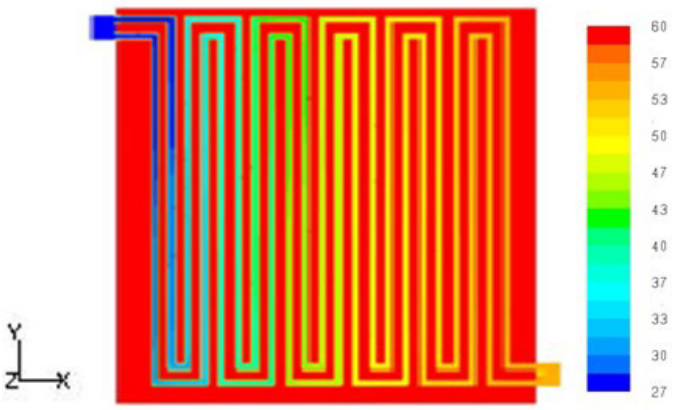

Fig. 4 Temperature (°C) distribution in flow field plate

4.4 Effect of methanol concentration on methanol and water crossover

From Fig.5a, it is seen that the methanol crossover rate increases with increase in methanol concentration. Methanol crossover current density decreases with increasing cell current density, but the difference in methanol crossover current density with increasing cell current density is low. This indicates that the rate of methanol diffusion through the membrane is high. Higher the methanol crossover leads to high mixed potential. This affects the cell performance and fuel utilization efficiency. Fig.5b shows the effect of methanol concentration on water generation in cathode and is represented in terms of water transfer coefficient. Water generation decreases with increase in cell current density due to high consumption rate of methanol and water and low methanol crossover. Net water transfer coefficient decreases from 55 to 32 as the current density increases. It is observed that the methanol concentration does not have significant effect on water generation. From fig.6, it is seen that the water generation at the cathode is mainly due to water crossover and is high at high current density due to high diffusion rate and electro-osmotic drag. At 1M, 50% of water generation is due to methanol crossover at low current density and it decreases with increasing current density. As the methanol concentration decreases, water concentration is more in methanol solution and it leads to reduction in methanol crossover and increase in water crossover.

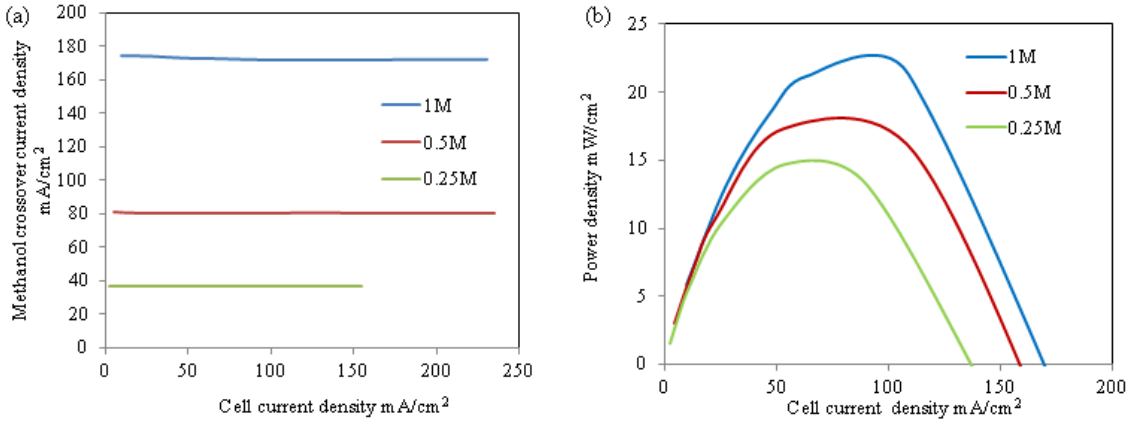

Fig.5 (a) Effect of methanol concentration on methanol crossover (b) Effect of methanol concentration on net water transfer coefficient

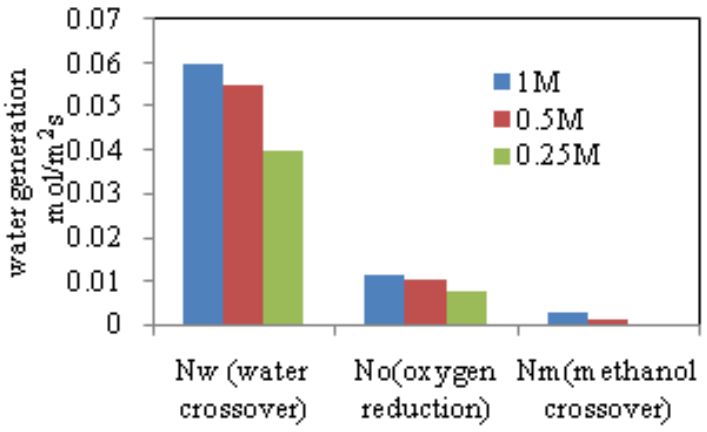

Fig.6 Effect of methanol concentration on water generation

4.5. Fuel utilization efficiency

Effect of methanol concentration on fuel utilization efficiency is shown in Fig.7a. At low concentration of 0.25M, FUE of 80% at 154 mA/cm^2 is obtained and is due to low methanol crossover. FUE increases with the cell current density due to high methanol consumption and low fuel loss. Even though the methanol crossover is high at 1M, FUE is 57% at 230 mA/cm^2. From Fig.7b, it is seen that the overall cell efficiency increases with decrease in methanol concentration due to high FUE. The maximum peak power density of 21 mW/cm^2 is obtained at 1 M with cell efficiency of 7% and 14 mw/cm^2 is obtained at 0.25 M with cell efficiency of 13%.

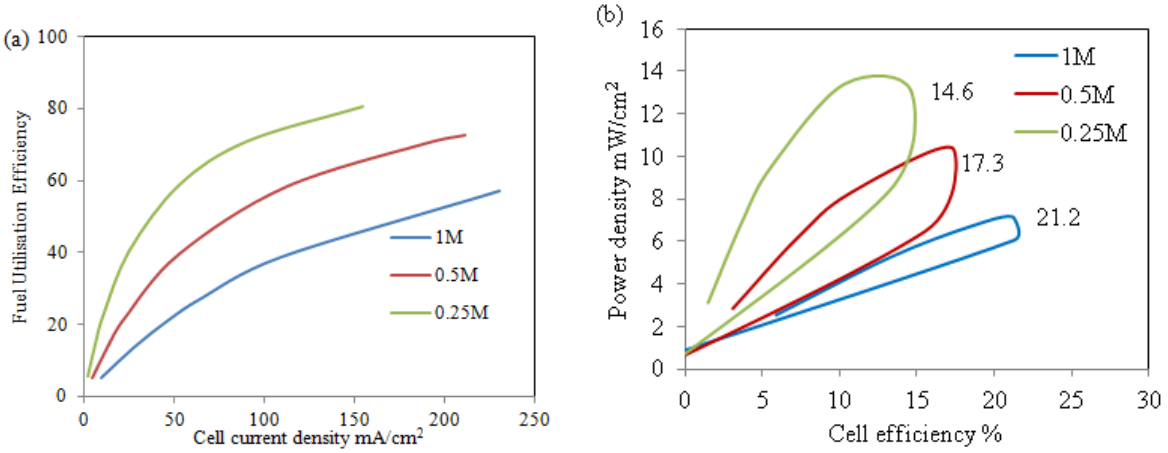

Fig.7 (a) Effect of methanol concentration on fuel utilization efficiency and (b) cell efficiency

5. Conclusions

A three dimensional non isothermal model is developed for anode side of DMFC. Methanol distribution in anode catalyst layer and membrane interface and temperature distribution in anode channel are found. Even though the methanol crossover is high at 1 M, the peak power density of 21 mW/cm^2 is obtained. The cell efficiency increases from 7 to 13% due to high FUE. The methanol concentration doesn't have significant impact on net water generation.

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