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CONTROL OF METHANOL CROSSOVER USING MICROPOROUS LAYER IN DIRECT METHANOL FUEL CELL

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ABSTRACT

A three dimensional model is developed to study the mass transfer processes of methanol and oxygen in Direct Methanol Fuel Cell (DMFC). A commercial software 'Fluent' is used for computation. The mass transfer process with electrochemical reactions is coupled and solved using self-written user defined functions. The model is used to investigate the effect of Microporous layer (MPL) thickness on methanol crossover and cell performance. The performance of the cell is computed for different microporous layer. The model results show that the methanol crossover decreases with increasing MPL thickness. It is observed that the methanol crossover is reduced without affecting the cell performance at low current density and fuel utilization efficiency is enhanced due to decrease in fuel loss.

Key words: DMFC, Microporous layer, Methanol crossover current density, mixed potential

1. INTRODUCTION

Direct Methanol Fuel Cell is becoming an important and competing energy conversion device due to its simple structure and efficiency. Two major challenging issues for commercialization are methanol crossover and slow reaction kinetics. Methanol crossover affects the cell performance by mixed potential at cathode and fuel utilization. This can be reduced by providing mass transfer resistance between anode diffusion layer and anode catalyst layer using Microporous layer (MPL). Different models have been developed to study the effect operating conditions such as concentration, temperature and flow rate on methanol crossover [1-4]. Methanol crossover is controlled by porous plate of different materials [5]. The methanol flux diffuses through the membrane is controlled by diffusion of methanol through the porous plate. Microporous layer is used at anode to reduce methanol crossover. About 45% of methanol crossover is reduced. This enhances the fuel utilization efficiency [6]. Control of methanol crossover in DMFC is important to improve the cell efficiency and reduce fuel loss. In this work, effect of MPL on methanol crossover and cell performance is studied.

2. PHYSICAL MODEL

Geometry of physical domain is shown in fig.1. The model domain consists of :

Anode channel (ACH)
Anode diffusion layer (ADL)
Anode microporous layer (AMPL)
Anode catalyst layer (ACL)
Membrane (MEM)
Cathode catalyst layer (CCL)
Cathode diffusion layer (CDL)
Cathode channel (CCH)

The methanol flows through the anode channel and air flows through the cathode channel. The reactants flow direction is shown in fig.1. The dimension of physical domain is given in table.1.

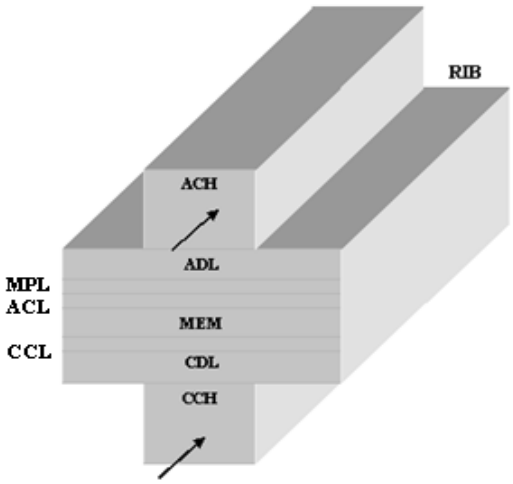

Fig. 1 Geometry of physical domain

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Table 1: Dimension of physical model [1]

Description	Value
Channel length (L_c)	5×10^{-2} m
Channel width (w_c)	1.0×10^{-3} m
Channel height (h_c)	8×10^{-4} m
Half rib width (w_r)	0.5×10^{-4} m
Diffusion layer thickness (t_d)	1.4×10^{-4} m
Catalyst layer thickness (t_c)	3×10^{-5} m
Membrane thickness (t_m)	1.8×10^{-4} m
Anode microporous layer thickness (AMPL)	4×10^{-5}m

2.1 Governing Equations

Governing equations of three dimensional model include mass, momentum and species conservation equations. These equations are fit for each domain of the model [1, 2]. Methanol transfers from channel to catalyst layer through diffusion layer.

Mass conservation equation:

$$\nabla(\rho u) = \dot{m} \qquad (1)$$

For other domains such as diffusion layers, channel and membrane

$$\dot{m} = 0$$

Table 2: Source terms used in ACL and CCL

Generation rate of mass	Source terms
$\dot{m} = M_{ch}\, S_{ch} + M_W S_W$	$S_{ch} = -\frac{ja}{6F}$
	$S_W = -\frac{ja}{6F}$
$\dot{m} = M_O S_O + M_W S_W$	$S_O = -\frac{jc}{4F}$
	$S_W = \frac{jc}{2F}$

Electrochemical reaction rate depends on the applied cell voltage or current. Methanol reacts with water produces CO_2 in ACL. Oxygen reduction reaction takesplace in CCL. Source terms used in catalyst layer are given in table.2. Source terms used depends on mass generation rate or consumption rate of species.

Momentum conservation equation:

$$\frac{1}{\varepsilon^2}\nabla.(\rho u u) = -\nabla P + \frac{1}{\varepsilon}\nabla.\mu(\nabla u) + Su \qquad (2)$$

$$Su = -\left(\frac{\mu u}{K}\right) \qquad (3)$$

S_u is source term used in porous layer. μ is viscosity of methanol and air, ε is porosity of diffusion layer and catalyst layer. For channel ε=1. Various parameters used in the model are found from elsewhere [1].

Species conservation equation:

$$\nabla\left(\rho u X_i\right) = \nabla\left(\rho D^{eff} \nabla X_i\right) + Si \qquad (4)$$

X_i , S_i are mass fraction and source terms of species respectively

Electrochemical reaction rate and volumetric current density relation is given by Tafel kinetic expression [1]. Reaction rate defines the current density of the cell. For a given value of current density, concentration of methanol at ACL is computed. The value of anode potential η_a is determined from,

$$j_a = a i_a^{ref} \left(\frac{C_{ch}}{C_{ch}^{ref}}\right) \exp\left(\frac{\alpha_a F}{RT}\eta_a\right) \qquad (5)$$

Average current density of the cell is given by

$$I = \int j_a dz \qquad (6)$$

Methanol flux crosses through the membrane [1] is given by,

$$N_{ch}^{m} = \frac{\lambda_{ch} I}{F} + \frac{\varepsilon D^{m}_{ch} C_{ch}^{ac/m}}{t_d} \qquad (7)$$

$C_{ch}^{ac/m}$ is the concentration of methanol at the ACL and membrane interface

First term represents electro-osmotic drag and second term is methanol diffusion due to concentration difference. Methanol concentration at CCL reacts with oxygen produces co_2. Methanol at CCL is zero due to complete oxidation.

The methanol crossover current density is given by [2]

$$I_{cr} = 6F N_{ch}^{m} \qquad (8)$$

Performance of the cell is controlled by limiting current density. It is the maximum current density obtained by the cell. The concentration at the ACL is approximately equal to zero and is given by,

$$I_l = \frac{6FC_b}{\left(\frac{t_d}{D_{ch}^{eff}} + \frac{1}{k}\right)} \qquad (9)$$

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C_b is bulk concentration, td diffusion layer thickness Convective mass transfer from channel to diffusion layer is equal to diffusive mass transfer in diffusion layer. Convective mass transfer coefficient is found from,

$$k = \frac{D_{ch}^{eff}\left(\frac{dXi}{dx}\right)}{X_d - X_b} \quad (10)$$

Volumetric current density at cathode and cathode potential relation is given by,

$$(I + I_c)\frac{1}{t_c} = ai_c^{ref}\left(\frac{C_O}{C_O^{ref}}\right)\exp\left(\frac{\alpha_c F}{RT}\eta_c\right)$$

$$j_c = ai_c^{ref}\left(\frac{C_O}{C_O^{ref}}\right)\exp\left(\frac{\alpha_c F}{RT}\eta_c\right) \quad (11)$$

Cell voltage and Polarization losses are given by,

$$V_c = V_o - \eta_a - \eta_c - IR_m \quad (12)$$

2.2 Assumptions and Boundary Conditions

Steady state, isothermal and single phase flow conditions are considered. The reactants flow in anode and cathode are laminar. Mass fraction and velocity of methanol are given as inlet condition in anode channel. Mass fraction and velocity of oxygen are given as inlet condition in cathode channel. Ambient pressure condition is given as outlet condition at the channel outlet. Mass fraction of methanol and air are set as zero at the channel outlet.

2.3 Solution Procedure

Mass, momentum and species conservation equations are solved using computational software "Fluent 6.3". Average current density, mass fraction and inlet velocity of methanol and oxygen are given as input. User defined function is used to incorporate diffusion coefficients and source terms. At a given cell current density, methanol concentration at ACL is computed. Depending on the methanol concentration at ACL and membrane, cell current density and methanol crossover current density are found. This process is repeated for different current density and the polarization curve is obtained at different methanol concentration. Convergence criterion set here is $1X10^{-6}$.

Geometry of the model is created and meshed in Gambit. Different mesh sizes are used for each domain of the model for grid independence study.

Grid independence test result is given in table.3. Average concentration at ACL for different grid sizes is computed. Percentage difference of concentration between successive grids is very less for 579600 cells. It is used for further computation.

Table 3: Grid independence study

Total no. of cells in the domain	**Average methanol concentration at ACL**	**% difference of concentration between successive grids**
579600	229.336	0.019
515200	229.292	0.025
422400	229.3518	0.267
266000	229.967	-

3. RESULTS AND DISCUSSIONS

3.1 Mass Fraction of Methanol in Anode

Distribution of methanol in anode side is shown in fig.2. Methanol is fed into the anode channel and diffuses through the diffusion layer to catalyst layer. There is slight variation in concentration difference along the anode channel. Concentration gradient is more at the anode diffusion layer and catalyst layer due to mass transfer resistance and methanol consumption. Methanol concentration is less under the rib region due to mass transport limitation. Depending on the applied cell current density, the methanol concentration at the ACL varies.

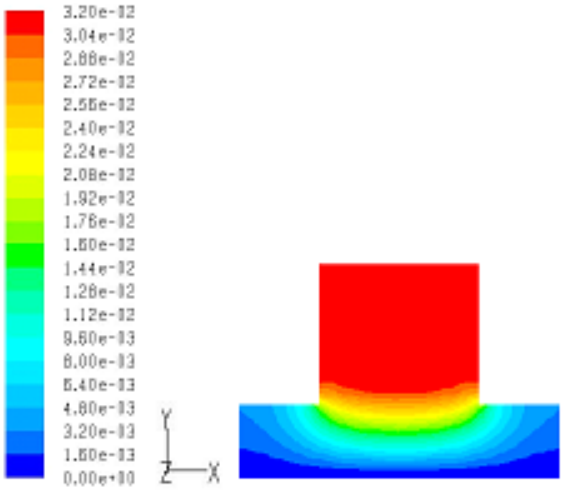

Fig.2. Mass fraction of methanol in anode

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3.2 Local Methanol Crossover Current Density

Methanol permeates through the membrane due to diffusion and electro-osmosis. Methanol crossover (MCO) current density at the interface between CCL and membrane is shown in fig.3. At the anode channel inlet, methanol concentration is more. It decreases as it moves along the channel direction due to methanol consumption. Depending on the methanol flux in membrane, methanol crossover current density is computed. At low current density, methanol diffusion rate is more. Hence the methanol crossover current density is more at low current density. It decreases as the cell current density increases.

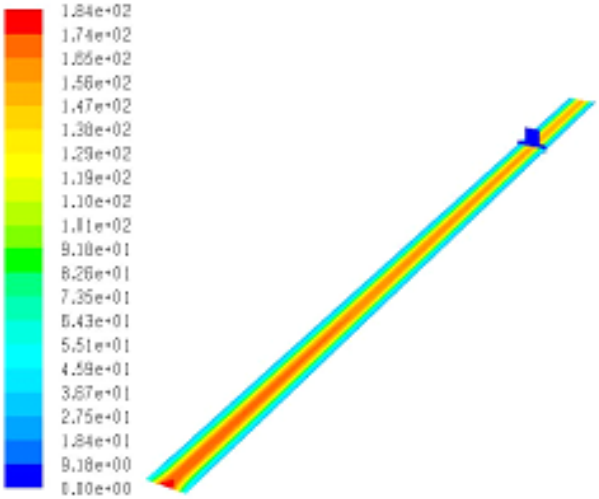

Fig.3. Methanol crossover current density at the interface between CCL and membrane in mA/cm^2

3.3 MODEL COMPARISON

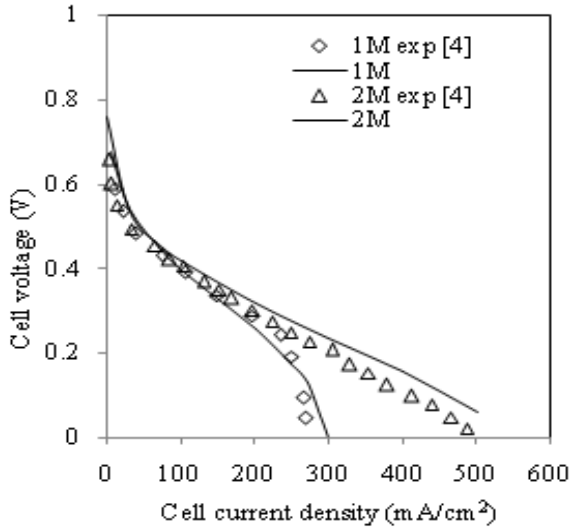

Fig.4. Comparison of cell performance

Comparison of model results is shown in fig.4. The design and operating conditions of experimental data at 1M and 2M are incorporated in the model. The model results are compared with experimental data [4] and show better agreement.

The model results are obtained for three different MPL thickness varying from 20 µm to 80µm. MPL is made of polytetrofloroethylene(PTFE) loading. Further increasing the thickness of MPL leads to crack [3]. It leads to further increase in methanol flux crosses through the membrane. Methanol oxidation takes place at CCL. This causes increase in cathode potential and affects the cell performance. For the thickest MPL, cathode potential is reduced by decrease in methanol crossover. The influence of MPL on methanol crossover and fuel utilization efficiency (FUE) is shown in fig.5 & 6. Methanol crossover rate in Membrane Electrode Assembly (MEA) with and without MPL is compared. Methanol crossover is reduced by 10% throughout the cell performance using 80µm thick MPL. This improves the cell performance with reduced cathode potential or mixed potential loss. Fuel loss is reduced by thick microporous layer. Hence the FUE is increased upto 3%. Effect of MPL thickness on power density is shown in fig.7. Power density decreases from 63mW/cm^2 to 49mW/cm^2 as the thickness of MPL increases.

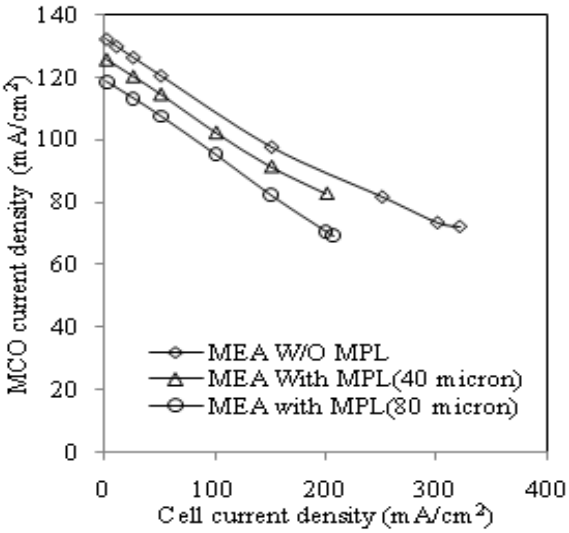

Fig.5. Effect of MPL on methanol crossover current density

The effect of MPL thickness on cell performance is shown in fig.8. At low current density upto 150 mA/cm^2, the performance is not affected by MPL due to reduction in MCO. As the thickness increases, the limiting current density is reduced due to mass transfer resistance.

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Depending on the MPL thickness, limiting current density is reduced from 320mA/cm^2 to 200 mA/cm^2. There is no sufficient methanol available at the ACL for current generation.

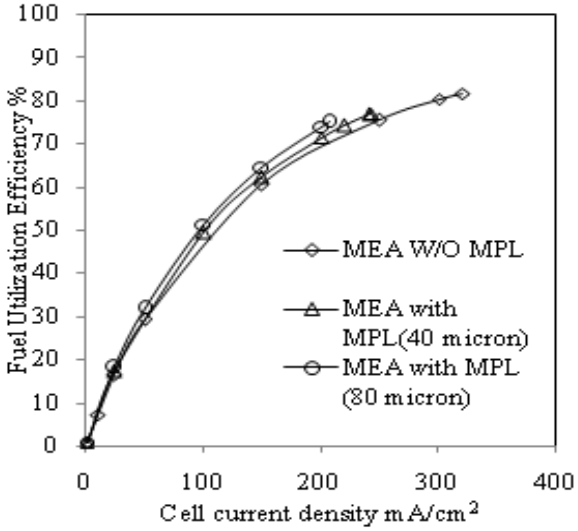

Fig.6 Influence of MPL on FUE

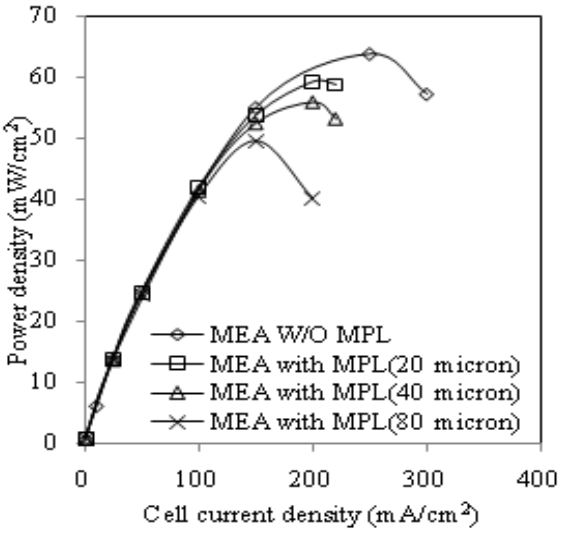

Fig.7 Effect of MPL on power density

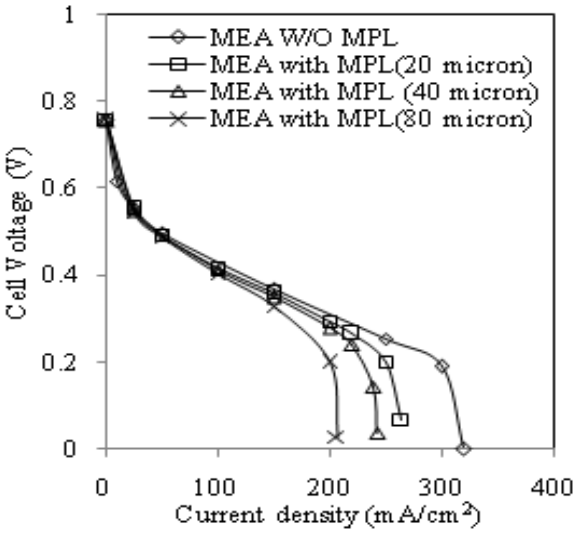

Fig.8 Effect of MPL on cell performance

4. CONCLUSIONS

In this work, a three dimensional model of DMFC is developed to study the effect of MPL thickness on cell performance. About 10% of methanol crossover current density is reduced by providing 80µm thick microporous layer. FUE is enhanced upto 3%. Limiting current density is decreased from 320 mA/cm^2 to 200mA/cm^2

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NOMENCLATURE

Symbol

C	Concentration	mol/m3
D	diffusion coefficient	(m^2 /s)
F	Faraday's constant	(C /mol)
I	current density	(A/ m^2)
j	transfer current density	(A/ m^3)
K	Permeability	(m^2)
M	molecular weight	(kg/ mol)
N	mole flux	(mol/ m^2 s)
R	Resistance	(Ω)
R_c	gas constant	(J /mol K)
S	source term	
T	temperature	(K)
V	velocity	(m/ s)
α	transfer coefficient	
ε	Porosity	
μ	viscosity	(kg /m s)
ρ	density	(kg/ m^3)
σ	conductivity	$(1/\Omega)m^{-1}$

Subscript

a	anode
C	cathode
Cr	methanol crossover
MEOH,ch	methanol
O	oxygen
Ref	reference

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Dr. Ajit Kumar Kolar is a professor at Department of Mechanical Engineering at IIT Madras. He has more than 30 years of teaching experience. His areas of research interest are Fuel cells, biomass combustion, advanced coal technologies, fluidised bed combustion and gasification of coal for power generation. He has several publications in international journals and conferences.

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