

Modeling and simulation of a direct methanol fuel cell anode

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Abstract

A mathematical model for the anode of a direct methanol fuel cell (DMFC) is presented. This model considers the mass transport in the whole anode compartment and the proton exchange membrane (PEM), together with the kinetic and ohmic resistance effects through the catalyst layer. The influence of key parameters on methanol crossover and anode performance is investigated. Our results indicate that, at low current density and high methanol concentration, the methanol crossover poses a serious problem for a DMFC. The anodic overpotential and reaction-rate distributions throughout the catalyst layer are more sensitive to the protonic conductivity than to the diffusion coefficient of methanol. Increasing the protonic conductivity can effectively enhance the performance of a DMFC.

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1. Introduction

The direct methanol fuel cell (DMFC) with proton exchange membrane (PEM) as electrolyte and liquid methanol/water solution as fuel is a promising power source for vehicular applications. However, there are still problems with high anodic overpotential and methanol crossover that inhibit its performance. Six electrons must be exchanged for methanol oxidation, which makes the oxidation kinetics inherently slower [1]. It has been shown that Pt-Ru materials possess substantially higher intrinsic activity than platinum alone [2–5], but even with this binary catalyst, the anodic overpotential in a DMFC is still much higher than that in a hydrogen cell. The problem of methanol crossover not only stands for the inefficient use of methanol but also brings about mixed potential at the cathode that adds further to the energy losses.

Methanol transport in a DMFC occurs by both diffusion and convection. Verbrugge [6] developed a simple diffusion model for methanol through a PEM, assuming the dilute solution theory. His model was validated by experimental data, which showed that the methanol diffusion through the membrane occurred nearly as readily as through water. Cruickshank and Scott [7] presented a simple model to describe the methanol crossover in a vapor feed DMFC and its effect on the cathodic overpotential. The measured

permeation rates of water and methanol through a Nafion[®] 117 membrane under varied pressure differentials across the PEM were used to determine the essential parameters in the model. This model has also been extended to include a one-dimensional model of the potential distribution and concentration distribution of methanol in the anode catalyst layer for a vapor feed DMFC [1,8]. Ren et al. [9] used a DMFC to experimentally determine the electro-osmotic drag of water in the membrane. At higher current densities, a linear relationship is found between the cell current and water flux across the fully hydrated membrane.

Baxter et al. [10] presented a model of the DMFC anode, which was considered to be a porous electrode. The pores were filled with methanol solution in which all species of the reaction were allowed to transport in the x -direction through the depth of electrode. Species movement in the pseudo y -direction was taken into account for water, methanol, and carbon dioxide. This model considered the catalyst layer only, however, a rather complex system of equations was necessary for this model. Scott et al. [11] described a model for the methanol transport processes that was used to predict the methanol concentration at the catalyst surface and thereby the anodic overpotential. This model, together with an empirical model of the open circuit voltage and the cathodic overpotential model, were used to predict the overall cell voltage, current density response of the fuel cell.

It is the purpose of this study to develop a mathematical framework to simulate the anode of a DMFC. This mathematical model considers the mass transport in the entire

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Nomenclature	
A_v	specific area of reaction surface (cm^2/cm^3)
$C_{\text{CH}_3\text{OH}}$	local methanol concentration (mol/cm^3)
$C_{\text{CH}_3\text{OH}}^{\text{an}}$	methanol concentration on anodic side of PEM (mol/cm^3)
$C_{\text{CH}_3\text{OH}}^{\text{cath}}$	methanol concentration on cathodic side of PEM (mol/cm^3)
$C_{\text{CH}_3\text{OH}}^{\text{f}}$	feed methanol concentration (mol/cm^3)
$C_{\text{CH}_3\text{OH}}^{\text{ref}}$	reference methanol concentration (mol/cm^3)
$C_{\text{CH}_3\text{OH}}^{\text{s}}$	methanol concentration at surface of diffusion layer (mol/cm^3)
$C_{\text{CH}_3\text{OH}}^0$	methanol concentration at $z = 0$ (mol/cm^3)
$C_{\text{H}_2\text{O}}$	local water concentration (mol/cm^3)
$C_{\text{H}_2\text{O}}^{\text{an}}$	water concentration on anodic side of PEM (mol/cm^3)
$C_{\text{H}_2\text{O}}^{\text{cath}}$	water concentration on cathodic side of PEM (mol/cm^3)
$\tilde{C}_{\text{CH}_3\text{OH}}$	derivative of $C_{\text{CH}_3\text{OH}}$ (mol/cm^4)
$\tilde{C}_{\text{CH}_3\text{OH}}^0$	value of $\tilde{C}_{\text{CH}_3\text{OH}}$ evaluated at $z = 0$ (mol/cm^4)
$D_{\text{CH}_3\text{OH}}^{\text{c,eff}}$	effective diffusion coefficient of methanol in catalyst layer (cm^2/s)
$D_{\text{CH}_3\text{OH}}^{\text{d}}$	bulk diffusion coefficient of methanol in water (cm^2/s)
$D_{\text{CH}_3\text{OH}}^{\text{d,eff}}$	effective diffusion coefficient of methanol in diffusion layer (cm^2/s)
$D_{\text{CH}_3\text{OH}}^{\text{m}}$	diffusion coefficient of methanol in PEM (cm^2/s)
$D_{\text{H}_2\text{O}}^{\text{m}}$	diffusion coefficient of water in PEM (cm^2/s)
F	Faraday's constant (96,500 C/mol)
i	protonic current density (A/cm^2)
$i_{0,\text{ref}}$	reference exchange current density (A/cm^2)
i^0	protonic current density at $z = 0$ (A/cm^2)
\tilde{i}	derivative of i (A/cm^3)
\tilde{i}^0	value of \tilde{i} evaluated at $z = 0$ (A/cm^3)
I	cell current density (A/cm^2)
k^{d}	mass transfer coefficient of methanol in diffusion layer (cm/s)
k^{f}	mass transfer coefficient of methanol from feed stream to diffusion layer (cm/s)
k^{m}	mass transfer coefficient of methanol in PEM (cm/s)
K_{m}	protonic conductivity of ionomer (S/cm)
$K_{\text{m}}^{\text{eff}}$	effective protonic conductivity in catalyst layer (S/cm)
K_{s}	electronic conductivity of solid phase (Pt-Ru/C) (S/cm)
$K_{\text{s}}^{\text{eff}}$	effective conductivity of solid phase in catalyst layer (S/cm)
ℓ_{c}	thickness of catalyst layer (cm)
ℓ_{d}	thickness of diffusion layer (cm)
ℓ_{m}	thickness of PEM (cm)
$M_{\text{H}_2\text{O}}$	molecular weight of water (18 g/mol)
$N_{\text{CH}_3\text{OH}}$	local methanol flux in catalyst layer ($\text{mol}/(\text{cm}^2 \text{ s})$)
$N_{\text{CH}_3\text{OH}}^{\text{d}}$	methanol flux through diffusion layer ($\text{mol}/(\text{cm}^2 \text{ s})$)
$N_{\text{CH}_3\text{OH}}^{\text{m}}$	methanol flux through PEM ($\text{mol}/(\text{cm}^2 \text{ s})$)
N_{diff}	water flux results from diffusion in PEM ($\text{mol}/(\text{cm}^2 \text{ s})$)
N_{drag}	water flux results from electro-osmotic drag in PEM ($\text{mol}/(\text{cm}^2 \text{ s})$)
$N_{\text{H}_2\text{O}}$	local water flux in catalyst layer ($\text{mol}/(\text{cm}^2 \text{ s})$)
$N_{\text{H}_2\text{O}}^{\text{d}}$	water flux through diffusion layer ($\text{mol}/(\text{cm}^2 \text{ s})$)
$N_{\text{H}_2\text{O}}^{\text{m}}$	water flux through PEM ($\text{mol}/(\text{cm}^2 \text{ s})$)
N_{T}	total flux of water and methanol in catalyst layer ($\text{mol}/(\text{cm}^2 \text{ s})$)
R	universal gas constant (8.3144 J/(mol K))
T	cell temperature (K)
v^{d}	superficial velocity of water in diffusion layer (cm/s)
v^{m}	superficial velocity of water in PEM (cm/s)
$x_{\text{CH}_3\text{OH}}$	mole fraction of methanol
<i>Greek symbols</i>	
α_{a}	anodic transfer coefficient
γ	order of reaction
ε^{d}	void fraction of diffusion layer
ε^{c}	void fraction of catalyst layer
$\varepsilon_{\text{s}}^{\text{c}}$	volume fraction of solid phase (Pt-Ru/C) in catalyst layer
$\varepsilon_{\text{m}}^{\text{c}}$	volume fraction of ionomer phase in catalyst layer
η	anodic overpotential (V)
$\lambda_{\text{H}_2\text{O}}$	electro-osmotic drag coefficient of water
$\rho_{\text{H}_2\text{O}}$	density of water ($1 \text{ g}/\text{cm}^3$)
ϕ_{m}	potential of the ionomer phase (V)
ϕ_{s}	potential of electronic conduction phase (V)

anode compartment and the PEM, together with the kinetic and ohmic resistance effects through the catalyst layer. The influence of the essential parameters on the methanol cross-over and anode performance is investigated.

2. Mathematical model

Fig. 1 presents a schematic of the anode bonded to a PEM in a DMFC. The system can be divided into three regions: a membrane region of solid polymer electrolyte (PEM), an active catalyst region (catalyst layer) that provides a catalytic site for the oxidation of methanol and a diffusion region (diffusion layer) composed of highly porous and electro-actively conductive material.

The diffusion layer is located adjacent to the flow channel plate and its open pores form transport avenues for the distribution of reactants to the catalyst layer and collection of carbon dioxide into the flow channel. The electronically conductive material conducts electrons generated at the

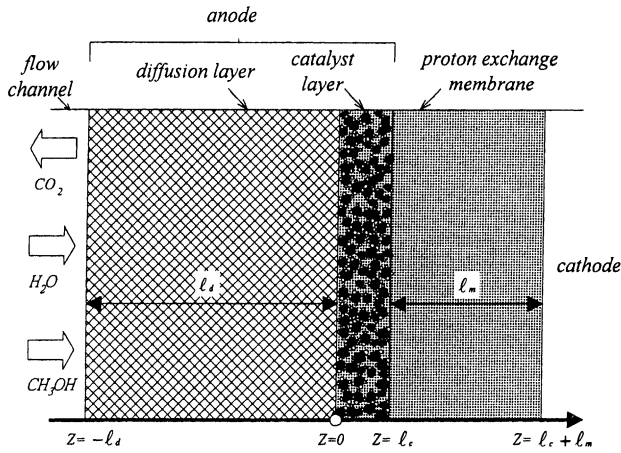


Fig. 1. Schematic diagram of the anode bonded to a PEM in a DMFC.

catalyst layer into the current collector. The catalyst layer is formed as a thin film of proton conductive ionomer (e.g. Nafion[®]) and a carbon-supported catalyst (e.g. Pt-Ru) uniformly dispersed in the ionomer. The protons produced at the catalyst layer are transported via migration through the PEM. Moreover, water and methanol are also transported through the PEM with the protons.

In this study, the anode of a single DMFC cell operated under steady-state isothermal conditions is considered and it is assumed that the anode and the cathode compartments have the same pressure. The model equations are defined in one direction (z -axis) through the anode and the PEM. The origin is set at the diffusion layer/catalyst layer interface. The modeling and assumptions for each individual region will be described in the following sections.

2.1. Methanol transport in the flow channel

The methanol concentration in the anode flow channel is defined as the feed concentration. The feed concentration decreases as the methanol solution flows down the stream. As the variation in the methanol concentration is small under general operating conditions, one can consider the feed concentration to be constant.

Carbon dioxide is generated in the anode electrode from the electrochemical reaction. Gas bubbles are then formed because of the moderate solubility of carbon dioxide in a methanol solution, and released into the flow channel. The released bubbles stir the flowing methanol solution, which complicates the methanol transport in the flow channel. The methanol transport from the feed stream to diffusion layer can be represented by

$$N_{\text{CH}_3\text{OH}}^{\text{d}} = k^{\text{f}} (C_{\text{CH}_3\text{OH}}^{\text{f}} - C_{\text{CH}_3\text{OH}}^{\text{s}}) \quad (1)$$

where $C_{\text{CH}_3\text{OH}}^{\text{f}}$ is the feed concentration of methanol, $C_{\text{CH}_3\text{OH}}^{\text{s}}$ the methanol concentration at the surface of the diffusion layer, and k^{f} is the mass transfer coefficient. The mass transfer at the gas-evolving electrode was measured for oxygen evolution at the vertical electrode by Fouad and

Sedahmed [12]. Scott et al. [11] correlated the oxygen evolution data and proposed that the coefficient of methanol transport from the feed stream to the diffusion layer is expressed using the following empirical equation

$$k^{\text{f}} = 1.87 \times 10^{-4} \left(\frac{I}{0.003} \right)^{0.32} \quad (2)$$

where I is the current density of the fuel cell. In this study, Eq. (2) is adopted for the evaluation of methanol transport from the flow channel to the diffusion layer.

2.2. Mass transport in the diffusion layer

The diffusion layer is composed of inactive carbon and no electrochemical reaction is expected within this region. Therefore, the water and methanol flux remains constant throughout this region. After passing through the diffusion layer, the water is consumed partly by the electrochemical reaction in the catalyst layer. The remaining water then migrates further through the PEM by electro-osmosis and diffusion. The water flux through diffusion layer is denoted as

$$N_{\text{H}_2\text{O}}^{\text{d}} = \frac{I}{6F} + N_{\text{H}_2\text{O}}^{\text{m}} \quad (3)$$

where F is Faraday's constant, and $N_{\text{H}_2\text{O}}^{\text{m}}$ is the water flux through the PEM, which will be derived in the PEM modeling in Section 2.4.

The methanol transport in the diffusion layer is a combination of diffusion and convection; therefore the methanol flux through the diffusion layer can be expressed as [13]

$$N_{\text{CH}_3\text{OH}}^{\text{d}} = -D_{\text{CH}_3\text{OH}}^{\text{d,eff}} \frac{dC_{\text{CH}_3\text{OH}}}{dz} + x_{\text{CH}_3\text{OH}} N_{\text{T}} \quad (4)$$

in which $D_{\text{CH}_3\text{OH}}^{\text{d,eff}}$ is the effective diffusion coefficient of methanol in the diffusion layer, $x_{\text{CH}_3\text{OH}}$ is the local mole fraction of methanol, and N_{T} is the total water and methanol flux. The effective diffusion coefficient of methanol can be derived from the bulk diffusion coefficient $D_{\text{CH}_3\text{OH}}^{\text{d}}$ and the void fraction of the diffusion layer, ε^{d} , using Bruggeman's correction [14–16].

$$D_{\text{CH}_3\text{OH}}^{\text{d,eff}} = (\varepsilon^{\text{d}})^{3/2} D_{\text{CH}_3\text{OH}}^{\text{d}} \quad (5)$$

As the concentration of methanol is low for the dilute methanol solution used in the DMFC, the total flux is approximately the flux of water only, and the local mole fraction of methanol $x_{\text{CH}_3\text{OH}}$ can be approximated by

$$x_{\text{CH}_3\text{OH}} = \frac{C_{\text{CH}_3\text{OH}}}{C_{\text{H}_2\text{O}} + C_{\text{CH}_3\text{OH}}} \cong \frac{C_{\text{CH}_3\text{OH}}}{C_{\text{H}_2\text{O}}} = \frac{M_{\text{H}_2\text{O}} C_{\text{CH}_3\text{OH}}}{\rho_{\text{H}_2\text{O}}} \quad (6)$$

where $M_{\text{H}_2\text{O}}$ and $\rho_{\text{H}_2\text{O}}$ are the molecular weight and density of water, respectively. Eq. (4) can be rewritten as

$$N_{\text{CH}_3\text{OH}}^{\text{d}} = -D_{\text{CH}_3\text{OH}}^{\text{d,eff}} \frac{dC_{\text{CH}_3\text{OH}}}{dz} + \frac{M_{\text{H}_2\text{O}} C_{\text{CH}_3\text{OH}}}{\rho_{\text{H}_2\text{O}}} N_{\text{H}_2\text{O}}^{\text{d}} \quad (7)$$

Assuming $D_{\text{CH}_3\text{OH}}^{\text{d,eff}}$ and $\rho_{\text{H}_2\text{O}}$ to be constant, Eq. (7) can be solved within the interval of $-\ell_d \leq z \leq 0$ and takes the form

$$N_{\text{CH}_3\text{OH}}^{\text{d}} = \frac{C_{\text{CH}_3\text{OH}}^{\text{s}} e^{v^{\text{d}}/k^{\text{d}}} - C_{\text{CH}_3\text{OH}}^0}{e^{v^{\text{d}}/k^{\text{d}}} - 1} v^{\text{d}} \quad (8)$$

where $k^{\text{d}} = D_{\text{CH}_3\text{OH}}^{\text{d,eff}}/\ell_d$, is the mass transfer coefficient in the diffusion layer, $C_{\text{CH}_3\text{OH}}^0$ the methanol concentration at the diffusion layer/catalyst layer interface (i.e. at $z = 0$), and $v^{\text{d}} = M_{\text{H}_2\text{O}} N_{\text{H}_2\text{O}}^{\text{d}}/\rho_{\text{H}_2\text{O}}$ is the superficial velocity of water in the diffusion layer.

Combining Eqs. (1) and (8), one can eliminate $C_{\text{CH}_3\text{OH}}^{\text{s}}$ and express the methanol flux through the diffusion layer using the feed concentration, $C_{\text{CH}_3\text{OH}}^{\text{f}}$ as

$$N_{\text{CH}_3\text{OH}}^{\text{d}} = \frac{C_{\text{CH}_3\text{OH}}^{\text{f}} e^{v^{\text{d}}/k^{\text{d}}} - C_{\text{CH}_3\text{OH}}^0}{e^{v^{\text{d}}/k^{\text{d}}} ((v^{\text{d}}/k^{\text{d}}) + 1) - 1} v^{\text{d}} \quad (9)$$

2.3. Catalyst layer

The rate of the electrochemical reaction in the catalyst layer can be described using a Butler–Volmer rate expression. This is then simplified to give a Tafel type equation in terms of the methanol concentration as

$$\frac{di}{dz} = A_v i_{0,\text{ref}} \left(\frac{C_{\text{CH}_3\text{OH}}}{C_{\text{CH}_3\text{OH}}^{\text{ref}}} \right)^{\gamma} \exp\left(\frac{6\alpha_a F \eta}{RT}\right) \quad (10)$$

where i is the local protonic current density, A_v the specific area of the reaction surface, $i_{0,\text{ref}}$ the reference exchange current density, γ the order of reaction, $C_{\text{CH}_3\text{OH}}$ the local methanol concentration, $C_{\text{CH}_3\text{OH}}^{\text{ref}}$ the reference methanol concentration, which is associated with $i_{0,\text{ref}}$, α_a the anodic transfer coefficient, and η is the anodic overpotential.

In this region, both water and methanol move in the z -direction due to the diffusion and electro-osmotic drag. The methanol transport in the catalyst layer is similar to that in the diffusion layer, so the local methanol flux can be expressed in a similar fashion as Eq. (7)

$$N_{\text{CH}_3\text{OH}} = -D_{\text{CH}_3\text{OH}}^{\text{c,eff}} \frac{dC_{\text{CH}_3\text{OH}}}{dz} + \frac{M_{\text{H}_2\text{O}} C_{\text{CH}_3\text{OH}}}{\rho_{\text{H}_2\text{O}}} N_{\text{H}_2\text{O}} \quad (11)$$

where $D_{\text{CH}_3\text{OH}}^{\text{c,eff}}$ is the effective diffusion coefficient of methanol in the catalyst layer, and $N_{\text{H}_2\text{O}}$ is the local water flux. The material balance for water gives

$$N_{\text{H}_2\text{O}} = \frac{I - i}{6F} + N_{\text{H}_2\text{O}}^{\text{m}} \quad (12)$$

The flux of methanol in the catalyst layer decreases along the z -axis due to its oxidation at the catalytic site, hence we have the material balance equation for methanol as

$$\frac{dN_{\text{CH}_3\text{OH}}}{dz} = -\frac{1}{6F} \frac{di}{dz} \quad (13)$$

The anodic overpotential at any location within the catalyst layer is defined as

$$\eta(z) = \phi_s(z) - \phi_m(z) \quad (14)$$

where $\phi_s(z)$ is the potential of the electronic conduction phase of the catalyst layer (i.e. the solid portion including carbon and catalyst particles), and $\phi_m(z)$ is the potential of the ionomer phase. Both $\phi_s(z)$ and $\phi_m(z)$ decrease in the z -direction, and Ohm's law equation for each phase can be written as

$$\frac{d\phi_s}{dz} = -\frac{1}{K_s^{\text{eff}}} (I - i) \quad (15)$$

$$\frac{d\phi_m}{dz} = -\frac{1}{K_m^{\text{eff}}} i \quad (16)$$

where K_s^{eff} and K_m^{eff} denote the effective conductivities of the solid phase and the ionomer phase, respectively. Therefore, the variation of the overpotential within the catalyst layer is given by

$$\frac{d\eta}{dz} = \left(\frac{1}{K_m^{\text{eff}}} + \frac{1}{K_s^{\text{eff}}} \right) i - \frac{1}{K_s^{\text{eff}}} I \quad (17)$$

2.4. Mass transport in the PEM

The water transport through the PEM results from both the electro-osmotic drag and diffusion, i.e.

$$N_{\text{H}_2\text{O}}^{\text{m}} = N_{\text{drag}} + N_{\text{diff}} \quad (18)$$

where N_{drag} denotes the water flux caused by the electro-osmotic drag, which, at a constant cell temperature, is proportional to the cell current density I and can be expressed as

$$N_{\text{drag}} = \lambda_{\text{H}_2\text{O}} \frac{I}{F} \quad (19)$$

where $\lambda_{\text{H}_2\text{O}}$ is the electro-osmotic drag coefficient of the water, which, for a fully hydrated PEM, is dependent only on the temperature. N_{diff} results from the water concentration gradient in the PEM, and can be expressed as

$$N_{\text{diff}} = D_{\text{H}_2\text{O}}^{\text{m}} \frac{C_{\text{H}_2\text{O}}^{\text{an}} - C_{\text{H}_2\text{O}}^{\text{cath}}}{\ell_m} \quad (20)$$

where $D_{\text{H}_2\text{O}}^{\text{m}}$ is the diffusion coefficient of the water in the PEM, ℓ_m the thickness of the PEM, $C_{\text{H}_2\text{O}}^{\text{an}}$ and $C_{\text{H}_2\text{O}}^{\text{cath}}$ are the water concentrations on the anodic and cathodic sides, respectively. It is appropriate to assume that the anodic side of the PEM retains a water saturation state. For a DMFC operated at current densities higher than a critical value, enhanced cathodic water accumulation due to the electro-osmotic drag and cathodic reaction could raise the water concentration on the cathodic side into a fully hydrated state [9]. For simplicity, we assumed both the anodic and cathodic sides of the PEM to be fully hydrated, eliminating the water diffusive transport, and $N_{\text{H}_2\text{O}}^{\text{m}}$ can be approximated by

$$N_{\text{H}_2\text{O}}^{\text{m}} \cong \lambda_{\text{H}_2\text{O}} \frac{I}{F} \quad (21)$$

The methanol is transported through the PEM in the same way as it is transported through the diffusion layer, so the

methanol flux through the PEM (i.e. methanol crossover) can be expressed in a similar form as shown in Eq. (8)

$$N_{\text{CH}_3\text{OH}}^m = \frac{C_{\text{CH}_3\text{OH}}^{\text{an}} e^{v^m/k^m} - C_{\text{CH}_3\text{OH}}^{\text{cath}}}{e^{v^m/k^m} - 1} v^m \quad (22)$$

where $k^m = D_{\text{CH}_3\text{OH}}^m/\ell_m$ is the mass transfer coefficient of methanol in the PEM, $v^m = M_{\text{H}_2\text{O}} N_{\text{H}_2\text{O}}^m/\rho_{\text{H}_2\text{O}}$, is the superficial velocity of the water in the PEM, $C_{\text{CH}_3\text{OH}}^{\text{an}}$ and $C_{\text{CH}_3\text{OH}}^{\text{cath}}$ denote the methanol concentration on the anodic and cathodic sides of the PEM, respectively. Due to oxidation and evaporation, the methanol concentration at the cathodic side is small, so we assumed that $C_{\text{CH}_3\text{OH}}^{\text{cath}}$ is zero and Eq. (22) becomes

$$N_{\text{CH}_3\text{OH}}^m = \frac{C_{\text{CH}_3\text{OH}}^{\text{an}} e^{v^m/k^m}}{e^{v^m/k^m} - 1} v^m \quad (23)$$

3. Solution procedure

By differentiating Eq. (11) with respect to z and combining it with Eqs. (12) and (13), we obtain

$$D_{\text{CH}_3\text{OH}}^{\text{c,eff}} \frac{d^2 C_{\text{CH}_3\text{OH}}}{dz^2} = \frac{M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \left(\frac{I-i}{6F} + N_{\text{H}_2\text{O}}^m \right) \frac{dC_{\text{CH}_3\text{OH}}}{dz} + \left(1 - \frac{M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} C_{\text{CH}_3\text{OH}} \right) \frac{1}{6F} \frac{di}{dz} \quad (24)$$

Again, differentiating Eq. (10) with respect to z and substituting $d\eta/dz$ into the so-obtained equation with the right-hand side of Eq. (17) yields

$$\frac{d^2 i}{dz^2} = \left\{ \frac{\gamma}{C_{\text{CH}_3\text{OH}}} \frac{dC_{\text{CH}_3\text{OH}}}{dz} + \frac{6\alpha_a F}{RT} \left[\left(\frac{1}{K_m^{\text{eff}}} + \frac{1}{K_s^{\text{eff}}} \right) i - \frac{I}{K_s^{\text{eff}}} \right] \right\} \frac{di}{dz} \quad (25)$$

There are two dependent variables, i and $C_{\text{CH}_3\text{OH}}$, involved in two second-order equations, Eqs. (24) and (25). These two equations can be transformed into a fourth-order system of first-order equations as

$$\frac{di}{dz} = \tilde{i} \quad (26)$$

$$\frac{dC_{\text{CH}_3\text{OH}}}{dz} = \tilde{C}_{\text{CH}_3\text{OH}} \quad (27)$$

$$\frac{d\tilde{i}}{dz} = \left\{ \frac{\gamma}{C_{\text{CH}_3\text{OH}}} \tilde{C}_{\text{CH}_3\text{OH}} + \frac{6\alpha_a F}{RT} \left(\frac{1}{K_m^{\text{eff}}} + \frac{1}{K_s^{\text{eff}}} \right) i - \frac{6\alpha_a F}{RT} \frac{I}{K_s^{\text{eff}}} \right\} \tilde{i} \quad (28)$$

$$\frac{d\tilde{C}_{\text{CH}_3\text{OH}}}{dz} = \frac{M_{\text{H}_2\text{O}}}{D_{\text{CH}_3\text{OH}}^{\text{c,eff}} \rho_{\text{H}_2\text{O}}} \left(\frac{I-i}{6F} + N_{\text{H}_2\text{O}}^m \right) \tilde{C}_{\text{CH}_3\text{OH}} + \left(1 - \frac{M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} C_{\text{CH}_3\text{OH}} \right) \frac{1}{D_{\text{CH}_3\text{OH}}^{\text{c,eff}} 6F} \tilde{i} \quad (29)$$

where \tilde{i} and $\tilde{C}_{\text{CH}_3\text{OH}}$ stands for the first derivatives of i and $C_{\text{CH}_3\text{OH}}$, respectively.

Four equations are presented for the four dependent variables: i , \tilde{i} , $C_{\text{CH}_3\text{OH}}$, $\tilde{C}_{\text{CH}_3\text{OH}}$. If their values at $z = 0$ (i.e. i^0 , \tilde{i}^0 , $C_{\text{CH}_3\text{OH}}^0$, and $\tilde{C}_{\text{CH}_3\text{OH}}^0$) are designated, the nonlinear first-order initial-value problem can be solved to yield the i , \tilde{i} , $C_{\text{CH}_3\text{OH}}$, $\tilde{C}_{\text{CH}_3\text{OH}}$ profiles using numerical methods (for example, the Runge–Kutta method [17]).

The diffusion layer is ionically insulated, so that the protonic current density must be zero at the diffusion layer/catalyst layer interface. Thus one gets

$$i^0 = 0 \quad (30)$$

Employing the balance of material, the methanol flux at the diffusion layer/catalyst layer interface is equal to $N_{\text{CH}_3\text{OH}}^d$, and one can write

$$N_{\text{CH}_3\text{OH}}^d = -D_{\text{CH}_3\text{OH}}^{\text{c,eff}} \tilde{C}_{\text{CH}_3\text{OH}}^0 + \frac{M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} C_{\text{CH}_3\text{OH}}^0 \left(N_{\text{H}_2\text{O}}^m + \frac{I}{6F} \right) \quad (31)$$

Equating Eqs. (31) and (9), we see that $\tilde{C}_{\text{CH}_3\text{OH}}^0$ is related to $C_{\text{CH}_3\text{OH}}^0$ and hence there are only two initial values i^0 , $C_{\text{CH}_3\text{OH}}^0$ remaining to be determined.

At the catalyst layer/PEM interface, the protonic current density must be equal to the cell current density I . Moreover, the methanol flux through the diffusion layer/catalyst layer interface is partly consumed in the catalyst layer and the rest migrates through the PEM as methanol crossover. The chosen i^0 , $C_{\text{CH}_3\text{OH}}^0$ must make the solution profiles satisfy the following two conditions

$$i(\ell_c) = I \quad (32)$$

$$N_{\text{CH}_3\text{OH}}^m + \frac{I}{6F} = -D_{\text{CH}_3\text{OH}}^{\text{c,eff}} \tilde{C}_{\text{CH}_3\text{OH}}^0 + \frac{M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} C_{\text{CH}_3\text{OH}}^0 \left(N_{\text{H}_2\text{O}}^m + \frac{I}{6F} \right) \quad (33)$$

in which the methanol crossover $N_{\text{CH}_3\text{OH}}^m$ is evaluated using Eq. (23). This consequently results in a shooting problem in terms of the two initial values i^0 and $C_{\text{CH}_3\text{OH}}^0$, which can be solved using the appropriate shooting technique. After obtaining the solutions to the initial-value problem, the profiles of i and $C_{\text{CH}_3\text{OH}}$ can be substituted into Eq. (10) to yield the spatial variation of the overpotential η through the catalyst layer.

4. Results and discussion

Fig. 2 compares the calculated anodic overpotential using our model with the experimental anodic overpotential given by Baxter et al. [10]. The experimental data were obtained from a methanol fed, polymer–electrolyte fuel cell operated with a hydrogen-producing cathode that was treated as a reversible hydrogen electrode (RHE) by supplying it with hydrogen gas at 1 atm. The methanol concentration at the diffusion layer/catalyst layer interface was set to 2 M. The measured voltages from the methanol/hydrogen fuel

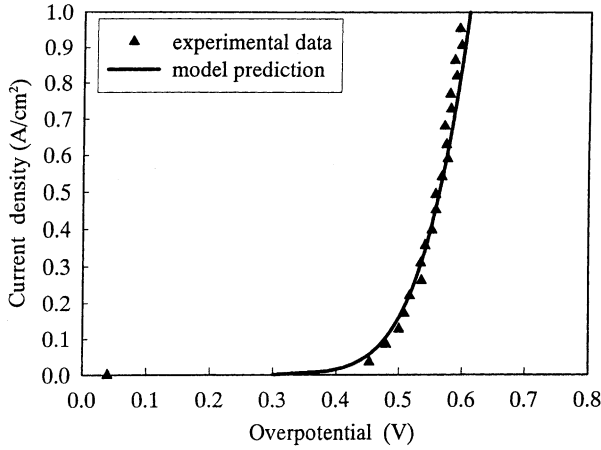


Fig. 2. Anodic polarization of a DMFC. The experimental data correspond to the methanol oxidation data of Baxter et al. [10], Pt-Ru catalyst (90:10 mol%), 2 M methanol feed.

cell were corrected to reflect the anodic overpotential. (In such a fuel cell, the cathodic overpotential is minimized and the anodic overpotential can be expressed as the total overpotential subtracted by the ohmic overpotential across the membrane.) Good agreements were obtained except at very low current densities, which is due primarily to the Tafel kinetic assumption. The parameter values used for calculation are given in Table 1. The effective values for the catalyst layer, $D_{\text{CH}_3\text{OH}}^{\text{c,eff}}$, K_m^{eff} , K_s^{eff} , are derived from their bulk values using Bruggeman's correction shown in Eq. (5). The rest of them are assumption values unless otherwise noted. The parameter values given in Table 1 are regarded as the base-case values in the following simulations.

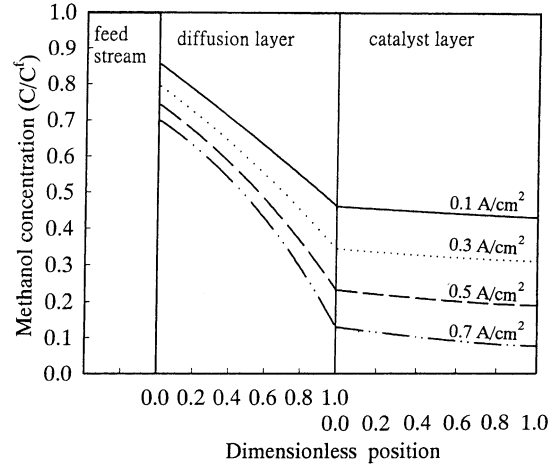


Fig. 3. Predicted variation of methanol concentration within the diffusion layer and the catalyst layer for various current densities and base-case conditions.

Fig. 3 shows the methanol concentration profiles in the diffusion layer and the catalyst layer for various current densities. As the current density of the cell increases, the methanol concentration decreases accordingly. At lower current densities, diffusion dominates the mass transport of methanol and only a fraction of methanol is consumed in the catalyst layer by the electrochemical reaction, therefore the concentration profiles are nearly linear. It should be noted that, even at high current densities, the drop in the methanol concentration through the catalyst layer is not as drastic as the oxygen concentration drop in the cathodic catalyst layer depicted in the article by Bernardi and Verbrugge [18]. This is due to the contribution of the methanol convection resulting

Table 1
Base-case parameter values

Parameter	Value
Anodic transfer coefficient, α_a	0.14
Cell temperature, T (K)	353
Reference exchange current density times area, $A_v i_{0,\text{ref}}$ (A/cm^3)	2.5×10^{-4}
Electro-osmotic drag coefficient of water, $\lambda_{\text{H}_2\text{O}}$	3.16 [9]
Order of reaction, γ	0.25
Catalyst layer thickness, ℓ_c (cm)	0.001
Diffusion layer thickness, ℓ_d (cm)	0.03
PEM thickness, ℓ_m (cm)	0.015
Feed methanol concentration, $C_{\text{CH}_3\text{OH}}^f$ (mol/cm^3)	0.003
Reference methanol concentration, $C_{\text{CH}_3\text{OH}}^{\text{ref}}$ (mol/cm^3)	0.002
Void fraction of diffusion layer, ε	0.6
Diffusion coefficient of methanol in water, $D_{\text{CH}_3\text{OH}}^d$ (cm^2/s)	2.8×10^{-5} [1]
Diffusion coefficient of methanol in PEM, $D_{\text{CH}_3\text{OH}}^m$ (cm^2/s)	4.9×10^{-6} [1]
Volume fraction of solid phase (Pt-Ru/C) in catalyst layer, ε_s^c	0.6
Volume fraction of ionomer phase in catalyst layer, ε_m^c	0.08
Void fraction of catalyst layer, ε^c	0.32
Effective diffusion coefficient of methanol in catalyst layer, $D_{\text{CH}_3\text{OH}}^{\text{c,eff}}$ (cm^2/s)	5.2×10^{-6}
Protonic conductivity of ionomer, K_m (S/cm)	0.1416 [1]
Effective protonic conductivity in catalyst layer, K_m^{eff} (S/cm)	3.2×10^{-3}
Electronic conductivity of solid phase (Pt-Ru/C), K_s (S/cm)	8.13×10^6 [10]
Effective conductivity of solid phase in catalyst layer, K_s^{eff} (S/cm)	3.78×10^6

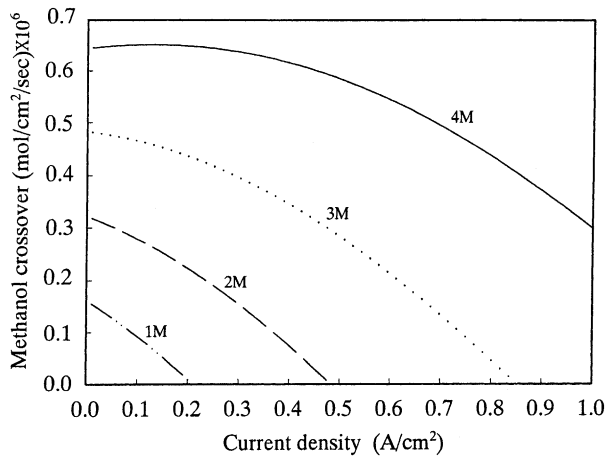


Fig. 4. Effect of current density on the methanol crossover for various feed concentrations.

from electro-osmosis with water, which is absent in the oxygen transport in the cathode.

Increasing the current density affects the methanol crossover in two conflicting ways. More water migrates through the PEM, but the methanol concentration that it takes along decreases, so the methanol crossover may either increase or decrease with the increasing current density. Fig. 4 illustrates the current density effects on the methanol crossover for various feed concentrations. We see that the methanol crossover decreases with increasing current density at feed concentrations lower than 3 M. However, at 4 M feed concentration, the methanol crossover increases slightly with increasing current density then decrease after it passes through a maximum.

If the methanol crossover is evaluated at a percentage of the total methanol flux, we can see the influence of the methanol crossover on the fuel efficiency of a DMFC. Fig. 5 shows the methanol crossover as a percentage of the total methanol flux transported from the feed stream into the electrode as a function of the operating current density. At

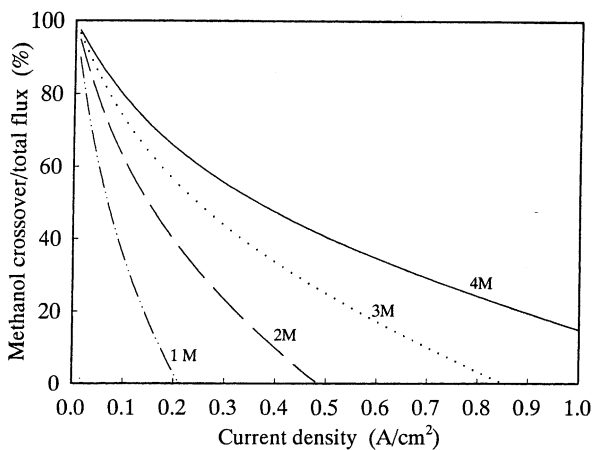


Fig. 5. Methanol crossover as a percent of the total methanol flux vs. cell current density for various feed concentrations.

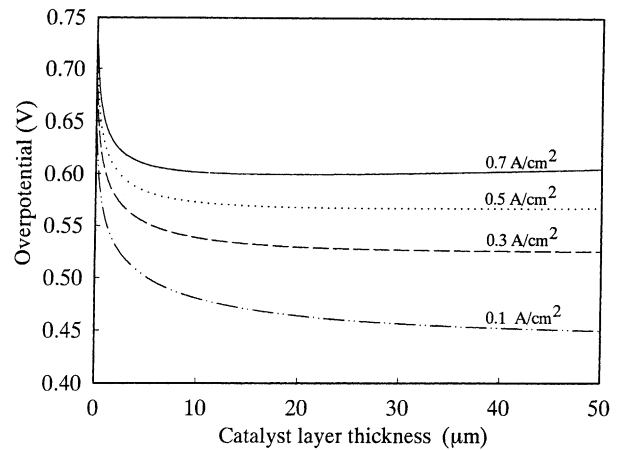


Fig. 6. Effect of catalyst layer thickness on the anodic overpotential for various current densities.

lower current densities, a large portion of the methanol fed into the fuel cell is wasted because of the methanol crossover. For feed concentrations higher than 2 M with a current density lower than 0.1 A/cm^2 , the crossover is more than 60% of the total methanol flux. The overall efficiency of a DMFC operated under such a condition may be no higher than 20%.

Fig. 6 shows the effects of the catalyst layer thickness on the anodic overpotential for four current densities. Because of the increase in catalyst surface area, the overpotential decreases with increasing catalyst layer thickness until a certain thickness, after that it levels off or even increases (e.g. 0.7 A/cm^2) with increasing thickness. This is explained by the fact that a thicker catalyst layer signifies a longer distance through which the current must flow and the ohmic potential drop resulting in an additional overpotential across the anode, especially when the current density is high. It is seen that for a DMFC operated under normal conditions, there may be no advantage in having an anode catalyst layer thicker than $10 \mu\text{m}$.

The mass transport of the reactants and products in the catalyst layer plays an important role in the electrode kinetics because it is related to species concentration at the catalytic site. The effective diffusion coefficient of methanol in the catalyst layer, $D_{\text{CH}_3\text{OH}}^{\text{c,eff}}$, affects the transport of methanol to the catalytic site and the effective protonic conductivity in the catalyst layer, K_m^{eff} , affects the proton transport away from where it is produced. Fig. 7 shows the spatial variations in reaction rate, di/dz , throughout the catalyst layer at a current density of 0.3 A/cm^2 for various $D_{\text{CH}_3\text{OH}}^{\text{c,eff}}$ and K_m^{eff} . For the base-case value, the reaction rate is higher in the front portion (near $z = \ell_c$) than in the back portion (near $z = 0$). The profile of the reaction rate is only slightly changed when $D_{\text{CH}_3\text{OH}}^{\text{c,eff}}$ is reduced to one-tenth of its base-case value, however, the reaction rate becomes fairly uniform throughout the catalyst layer when K_m^{eff} is increased to 10 times its base-case value. It is obvious that the reaction-rate distribution is more sensitive to the protonic conductivity than to the diffusion coefficient of methanol.

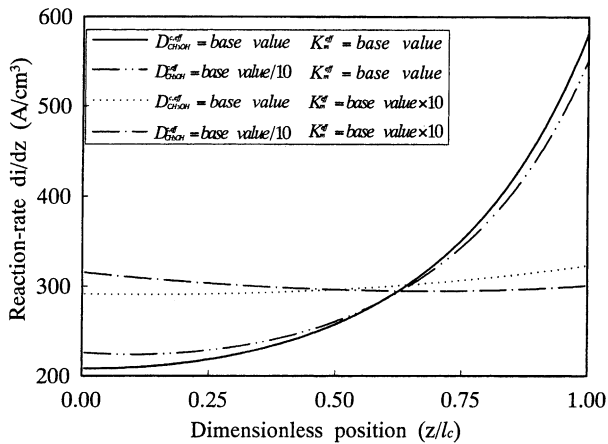


Fig. 7. Spatial variation of reaction rate throughout the catalyst layer for various $D_{CH_3OH}^{eff}$ and K_m^{eff} . The cell current density is 0.3 A/cm^2 .

When the electrochemical reaction occurs more uniformly throughout the catalyst layer, the catalyst can be utilized more efficiently, and this should result in higher fuel cell performance. Figs. 8 and 9 illustrate the variation in the anodic overpotential with the effective diffusion coefficient of methanol and protonic conductivity, respectively. From the flat lines in Fig. 8, we can infer that the variation in the effective methanol diffusion coefficient in the catalyst layer has almost no effect on the anodic overpotential of a DMFC. From Fig. 9, however, we see that the anodic overpotential can be substantially reduced if a catalyst layer with good effective protonic conductivity is applied. The difference in sensitivity may result from the fact that the effective protonic conductivity strongly governs the proton transport in the catalyst layer, while methanol diffusion is only a portion in methanol transport. This suggests that, in order to increase the effective protonic conductivity in the catalyst layer, the void volume in the catalyst layer (space among catalyst particles) should be filled with ionomer to a large extent.

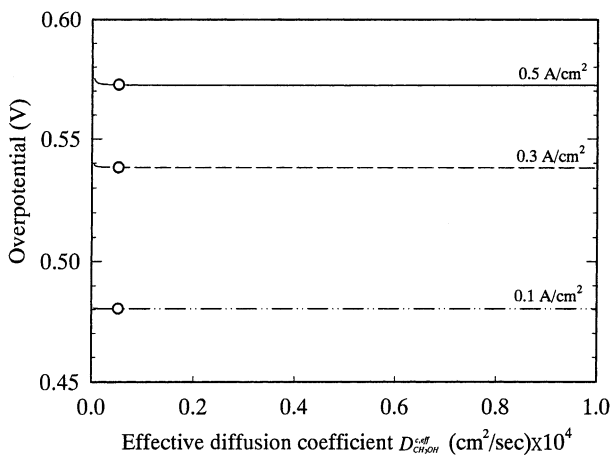


Fig. 8. Variation of anodic overpotential with $D_{CH_3OH}^{eff}$ for various current densities. The circles indicate the base-case values.

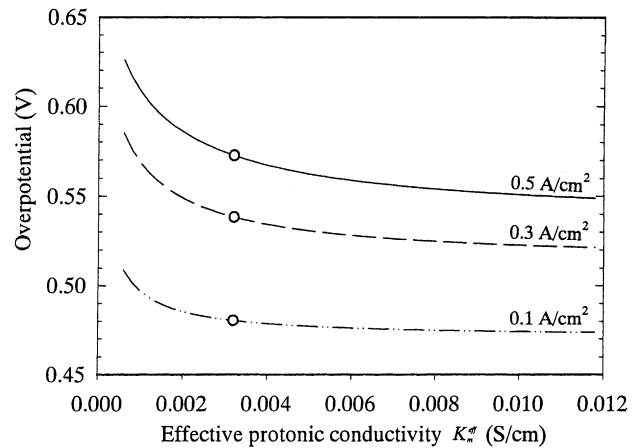


Fig. 9. Variation of anodic overpotential with K_m^{eff} for various current densities. The circles indicate the base-case values.

5. Conclusions

We developed a mathematical model for describing what happens in the anode compartment associated with the PEM. The formulated equation system was solved using the shooting technique to characterize the anode of a direct methanol fuel cell. The predicted polarization behavior compared well with experimental data from previous work. The results from this study show that, for a DMFC operated under low current density and high methanol feed concentration conditions, a large portion of the methanol fed into the fuel cell is wasted due to methanol crossover making low fuel efficiency inevitable. The thickness of the catalyst layer affects the anodic overpotential. Increasing the thickness of the catalyst layer may enhance the performance of a DMFC to a certain extent, but it is not advisable to have a thickness greater than $10 \mu\text{m}$. The reaction-rate distribution throughout catalyst layer is more sensitive to the effective protonic conductivity than to the effective diffusion coefficient of the methanol, hence increasing the effective protonic conductivity can effectively enhance the performance of a DMFC. This suggests that the void volume in the catalyst layer should be filled with ionomer to a large extent.

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