# Model-Based Design and Optimization of the Microscale Mass Transfer Structure in the Anode Catalyst Layer for Direct Methanol Fuel Cell

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*Microscale mass transfer structure in the anode catalyst layer (CL) can significantly alter the performance of a direct methanol fuel cell (DMFC) because it changes both the oxidation rate and crossover flux of methanol. The microscale mass transfer structure can be modified by changing the loading of the pore former (PF). An empirical model was developed for the microstructural design and optimization of anode CL by incorporating the PF into the anode CL. The optimal loading of PF is 100 g/m$^2$ according to the calculated results. Experimental results confirmed the accuracy of the calculations, and the passive DMFC performs 37% better by incorporating the optimal loading of PF into the anode CL as compared to the conventional anode CL. The validity of the proposed empirical model can also be proven by comparing the calculated polarization results with the previously reported experimental data.* © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 780–786, 2013

*Keywords: anode catalyst layer, direct methanol fuel cell, empirical model, microscale mass transfer, pore former*

## Introduction

Membrane electrode assembly (MEA) is the core of the direct methanol fuel cell (DMFC).[1] A typical MEA for the DMFC is fabricated by sandwiching a proton-exchange membrane (PEM) between the anode and cathode electrodes. Each electrode consists of a catalyst layer (CL) and a diffusion layer (DL).[2] The CL is where electrochemical reaction occurs and the DL provides mechanical support, good electrical conductivity, and uniform reactant distribution. Research on MEAs has been widely performed to improve the kinetic rate of methanol oxidation/oxygen reduction, to decrease the methanol crossover and to optimize the mass transfer in the DMFC. A great deal of work has been performed in the field of catalyst[3–6] and membrane development[7–9] to improve the kinetic rate. However, the performance of the MEA is also significantly dependent on the electrode structure and composition. For example, the dependence of the MEA performance on the catalyst and Nafion loadings in the anode/cathode CL has been repeatedly confirmed.[10–13] Recently, studies have focused on the mass transfer behavior of the reactants inside the electrodes.[14–16] To improve the mass transfer, pore formers (PFs)[17–21] were incorporated into the CLs or the microporous layers to improve the performance of the fuel cell. Tucker et al.[17] enhanced the maximum power density of an active DMFC from approximately 900 to 1200 W/m$^2$ by adding 50 wt % $Li_2CO_3$ into the anode CL as PF. Zhao et al.[18] used $NH_4HCO_3$, $(NH_4)_2SO_4$, and $(NH_4)_2C_2O_4$ as PFs to prepare the MEAs and discovered that $NH_4HCO_3$ enhanced the uniform dispersion of the catalysts on the surface of the electrode. $NH_4HCO_3$ was also used as a PF in the cathode CL of a DMFC, which improve the cell performance by approximately 30%. The performance enhancement obtained using PFs in a direct ethanol fuel cell was also confirmed by adding 10 wt % $NaHCO_3$ into the catalyst ink during MEA fabrication.[20] The effect of the PF loading in the anode CL of a DMFC was also investigated.[21] The results indicated that the cell performance can be enhanced by approximately 35% by adding a substantial amount of PF.

Although several studies indicate that the performance of the direct methanol/ethanol fuel cells can be improved by adding PF in CLs, the optimal loading of PF has never been studied by comprehensively understanding the effect of PF on microscale mass transfer structure and activity sites for fuel oxidation reactions. In this article, an empirical model was developed for PF ($NH_4HCO_3$) loading optimization in the anode CL of the DMFC and for the purpose of optimizing the microstructure of the anode CL in terms of the active area for methanol electro-oxidation and methanol transfer behavior. The results indicate that the addition of PF in the anode CL can modify the microstructure of the anode CL

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and further improve the DMFC performance. The optimal loading of PF in anode CL for both passive and active DMFCs, calculated in terms of the geometric area of the anode, is 100 g/m$^2$. The calculated polarization results of the passive/active DMFC with optimized anode CLs correlate well with the experimental data.

## Experimental

### *MEA preparation*

Four milligram per square centimeter PtRu/C (40 wt %, of Pt and Ru atomic ratio of Pt to Ru = 1:1), 1.8 mg/cm$^2$ Nafion (5 wt % Nafion solution), and a specified loading of ammonium hydrogen carbonate (AH) were dispersed in an aqueous solution of isopropyl alcohol with ultrasonic treatment. After the suspension was uniformly dispersed, we sprayed it onto carbon paper to form the anode. The cathode was formed by spraying 4.0 mg/cm$^2$ of Pt/C (40 wt % Pt, 1.8 mg/cm$^2$ Nafion as a binding agent) onto carbon paper. A Nafion 117 membrane (thickness 175 $\mu$m) was sandwiched between the anode and the cathode by hot pressing to form the MEA at 130°C and 2.0 MPa.

### *Fabrication and measurements of the passive DMFC*

MEAs with a geometric area of 2.0 cm × 2.0 cm (4.0 cm$^2$) were prepared for the fuel cell. In addition to the MEA, a passive DMFC included a fuel reservoir and anode/cathode current collectors. Polycarbonate was selected as the fuel reservoir material, and the gold-electroplated 316 L stainless steel meshes were used as the current collectors. Polarization tests were performed on the Fuel Cell Test System (Arbin Instruments) at 25°C.

### *Model development and analysis*

*Basic Equations.* An empirical model was developed to adjust the PF loading in the anode CL to optimize the microstructure of the anode CL in the DMFC. Increased porosity of the anode CL as a result of PF incorporation can notably enhance the methanol diffusivity and also enlarge the active area for the methanol electrochemical reaction because the methanol oxidation reaction (MOR) occurs in the anode CL.

The mass transfer process of methanol in the anode of DMFC is schematized in Figure 1. We assume that MOR only takes place at the interface of the anode CL and PEM in the proposed model. Therefore, the methanol flux in the anode DL and anode CL should be equal, $J_{\mathrm{m,ad}} = J_{\mathrm{m,ac}}$. Meanwhile, the methanol concentration distribution along the $x$ direction in the anode CL can be determined according to the following equation

$$J_{\mathrm{m,ad}} = J_{\mathrm{m,ac}} = D_{\mathrm{m,ac}} \frac{dc_{\mathrm{m,ac}}}{dx} \tag{1}$$

where $c_{\mathrm{m,ac}}$ is the local methanol concentration and $D_{\mathrm{m,ac}}$ is the effective methanol diffusivity in anode CL. The value of $D_{\mathrm{m,ac}}$ correlates to the porosity of the anode CL, and the relationship can be expressed as follows

$$D_{\mathrm{m,ac}} = D_{\mathrm{m,L}} \varepsilon_{\mathrm{ac}}^{1.5} \tag{2}$$

$D_{\mathrm{m,L}}$ in Eq. 2 is the methanol diffusivity in liquid water. $\varepsilon_{\mathrm{ac}}$ is the adjusted porosity of the anode CL. The value of $\varepsilon_{\mathrm{ac}}$ can be calculated by dividing the total volume of the anode CL to the pore volume, and these two volumes are both dependent on the PF loading as follows

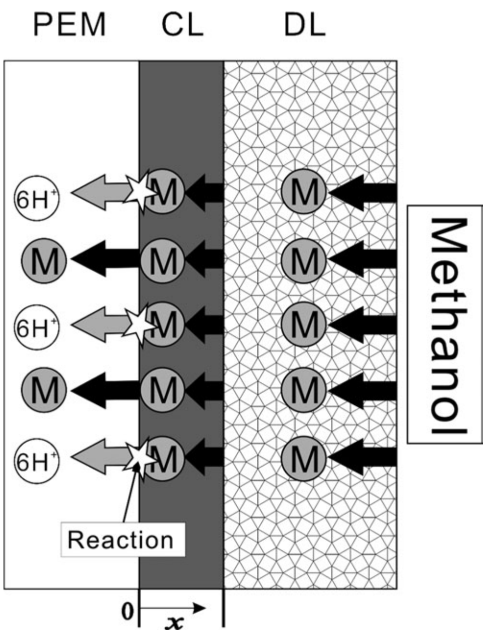

**Figure 1. A schematic diagram showing mass transfer in the anode of the DMFC.**

$$\varepsilon_{\mathrm{ac}} = \frac{V_{\mathrm{pore,tot}}}{V_{\mathrm{tot}}} = \frac{V_{\mathrm{pore,st}} + V_{\mathrm{pore,PF}}}{V_{\mathrm{st}} + V_{\mathrm{pore,PF}}} = \frac{\varepsilon_{\mathrm{st}} V_{\mathrm{st}} + \kappa A_{\mathrm{e}} s_{\mathrm{PF}}/\rho_{\mathrm{PF}}}{V_{\mathrm{st}} + \kappa A_{\mathrm{e}} s_{\mathrm{PF}}/\rho_{\mathrm{PF}}} \tag{3}$$

where $V_{\mathrm{pore,tot}}$ and $V_{\mathrm{tot}}$ are, respectively, the total volumes of the pores in the anode CL and of the anode CL itself. $V_{\mathrm{pore,st}}$ and $V_{\mathrm{pore,PF}}$ are, respectively, the volumes of the pores in the anode CL before the addition of the PF and of the pores produced by the PF. $\varepsilon_{\mathrm{st}}$ and $V_{\mathrm{st}}$ are the standard porosity and volume of the anode CL in absence of PF, respectively. $s_{\mathrm{PF}}$ and $\rho_{\mathrm{PF}}$ are the loading and density of the PF, respectively. $\kappa$ is the deformation coefficient of the anode CL during the PF decomposition. $A_{\mathrm{e}}$ is the electrode area used in the present model and its value is 1.0 m$^2$.

Methanol transferred through the anode CL is consumed by two paths: oxidation at the anode CL/PEM interface and crossover through the PEM to the cathode side. Therefore, the mass conservation equation for methanol in the anode CL can be obtained from the following

$$\frac{i}{6F} + J_{\mathrm{m,PEM}} = J_{\mathrm{m,ac}} \tag{4}$$

The first term on the left side of Eq. 4 represents the methanol consumed by electro-oxidation at the anode CL/PEM interface, and the second term represents the methanol crossover flux through the PEM. This mass conservation is demonstrated in Figure 1.

The anode polarization of the DMFC can be described by the following modified Butler–Volmer equation[22]

$$i_{\mathrm{a,v}} = i_0 \left[ \frac{c_{\mathrm{m}}^{\mathrm{ac}}}{c_{\mathrm{m}}^{\mathrm{ref}}} \exp\left( \frac{\alpha_{\mathrm{a}} F}{RT} \eta_{\mathrm{a}} \right) \right] \tag{5}$$

where $i_{\mathrm{a,v}}$ is the volume current density in the anode. $c_{\mathrm{m}}^{\mathrm{ac}}$ is the methanol concentration, and $\alpha_{\mathrm{a}}$ is the transfer coefficient in the anode CL. $i_0$ and $c_{\mathrm{m}}^{\mathrm{ref}}$ are the exchange current density and the reference methanol concentration in the anode CL, respectively.

*Model Analysis.* Equation 3 can be used to calculate the porosity variation in the anode CL with the PF loading. By combining Eq. 3 with Eq. 2, we obtain the following relationship between the methanol diffusivity and the PF loading in the anode CL

$$D_{\mathrm{m,ac}} = D_{\mathrm{m,L}} \left( \frac{\varepsilon_{\mathrm{ori}} V_{\mathrm{ori}} + \kappa s_{\mathrm{PF}}/\rho_{\mathrm{PF}}}{V_{\mathrm{ori}} + \kappa s_{\mathrm{PF}}/\rho_{\mathrm{PF}}} \right)^{1.5} \tag{6}$$

In Eq. 5, volume current density was used to describe the anode polarization of the DMFC. However, in an operating DMFC, only the surface current density can be set up. Therefore, derivation can be done on Eq. 5 to transform the volume current density $i_{\mathrm{a,v}}$ surface current density $i_{\mathrm{a}}$ by dividing a thickness $dx$ into the corresponding surface current density $di_{\mathrm{a}}(x)$. Meanwhile, the active surface area of the anode CL can be invited into the equation by relating it with the actual reference exchange current density in the anode CL $i_{\mathrm{ref}} = i_{\mathrm{ref,st}} \frac{a_{\mathrm{act}}}{a_{\mathrm{act,st}}}$. With these derivations, we can obtain a transformation of Eq. 5 as follows

$$\frac{di_{\mathrm{a}}(x)}{dx} = \frac{a_{\mathrm{act}}}{a_{\mathrm{act,st}}} i_{\mathrm{ref,st}} \left[ \frac{c_{\mathrm{m,ac}}}{c_{\mathrm{m,ref}}} \exp\left( \frac{\alpha_{\mathrm{a}} F}{RT} \eta_{\mathrm{a}} \right) \right] \tag{7}$$

where $i_{\mathrm{ref,st}}$ and $a_{\mathrm{act,st}}$ are the standard reference exchange current density and standard active surface area in the anode CL in absence of PF.

The boundary conditions of $i_{\mathrm{a}}$ $(x = 0) = 0$, and $i_{\mathrm{a}}$ $(x = \delta_{\mathrm{ac}}) = i$, as given in the literature,[22] are considered. $i$ is the operating current density of the DMFC. Using these two boundary conditions, Eq. 7 can be solved as follows

$$\eta_{\mathrm{a}} = \frac{RT}{\alpha_{\mathrm{a}} F} \ln \frac{i c_{\mathrm{m,ref}}}{a_{\mathrm{act}} i_{\mathrm{ref}} \delta_{\mathrm{ac}} c_{\mathrm{m,ac-PEM}}} \tag{8}$$

The subscript ac-PEM in Eq. 8 represents the anode CL/PEM interface. To obtain the relationship between $c_{\mathrm{m,ac-PEM}}$ and $i$, the methanol concentration distribution in the anode DL is assumed to be linear because no methanol is consumed in the anode DL. Hence, the methanol flux in the anode DL can hence be expressed as follows

$$\begin{aligned} J_{\mathrm{m,ad}} &= D_{\mathrm{m,ad}} \frac{c_{\mathrm{m,ch}} - c_{\mathrm{m,ac-ad}}}{\delta_{\mathrm{ad}}} \\ J_{\mathrm{m,ac}} &= D_{\mathrm{m,ac}} \frac{c_{\mathrm{m,ac-ad}} - c_{\mathrm{m,ac-PEM}}}{\delta_{\mathrm{ac}}} \end{aligned} \tag{9}$$

By combining Eq. 9 with Eq. 4, the relationship between $c_{\mathrm{m,ac\ -\ PEM}}$ and $i$ can be obtained as follows

$$c_{\mathrm{m,ac-ad}} = c_{\mathrm{m,ch}} - \left( \frac{i}{6F} + J_{\mathrm{m,PEM}} \right) \frac{\delta_{\mathrm{ad}}}{D_{\mathrm{m,ad}}} \tag{10}$$

The methanol crossover flux $J_{\mathrm{m,PEM}}$ consists of two parts: methanol diffusion produced by the concentration gradient of methanol in the PEM and the methanol flux due to the electro-osmosis drag. Therefore, the following equation can be obtained

$$J_{\mathrm{m,PEM}} = \frac{D_{\mathrm{m,PEM}} c_{\mathrm{m,ac-PEM}}}{\delta_{\mathrm{PEM}}} + \frac{M_{\mathrm{w}} \lambda_{\mathrm{w}} i}{\rho_{\mathrm{w}} F} c_{\mathrm{m,ac-PEM}} \tag{11}$$

where $D_{\mathrm{m,PEM}}$ is the methanol diffusivity in the PEM, $c_{\mathrm{m,ac\ -\ PEM}}$ is the methanol concentration at the anode CL/PEM interface, and $\delta_{\mathrm{PEM}}$ is the thickness of the PEM. $M_{\mathrm{w}}$, $\lambda_{\mathrm{w}}$, and $\rho_{\mathrm{w}}$ are the molecular weight, electro-osmotic drag coefficient, and density of water, respectively.

Before working out the unknown parameters in the aforementioned equations, it is necessary to express the relationship between $a_{\mathrm{act}}/D_{\mathrm{m,ac}}$ and $\varepsilon_{\mathrm{ac}}$ as the porosity of the anode CL can directly determine the value of $a_{\mathrm{act}}/D_{\mathrm{m,ac}}$

$$\begin{aligned} a_{\mathrm{act}} &= a_{\mathrm{act,st}} \times \frac{\varepsilon_{\mathrm{ac}}}{\varepsilon_{\mathrm{st}}} \\ D_{\mathrm{m,ac}} &= D_{\mathrm{m,w}} \times \varepsilon_{\mathrm{ac}} \end{aligned} \tag{12}$$

where $a_{\mathrm{act,st}}$ is the standard active surface area of the anode CL in absence of PF, which was obtained from the CO stripping experiment. It has nine unknown parameters in Eqs. 8–11: $\eta_{\mathrm{a}}$, $c_{\mathrm{m,ac-PEM}}$, $J_{\mathrm{m,PEM}}$, $c_{\mathrm{m,ac-ad}}$, $J_{\mathrm{m,ad}}$ ($J_{\mathrm{m,ac}}$), $i$, $a_{\mathrm{act}}$, $\delta_{\mathrm{ac}}$, and $D_{\mathrm{m,ac}}$. The values of $a_{\mathrm{act}}$ and $D_{\mathrm{m,ac}}$ were calculated from the value of the PF loading $s_{\mathrm{PF}}$ as demonstrated in Eq. 12. Therefore, when the operating current density $i$ is 600 A/m$^2$ and the PF loading is set at a certain value, there are five unknown parameters in the equation set that can be obtained using the five equations in the equation set.

By varying the PF loading from 0 to 300 g/m$^2$ and fixing the operating current density at 600 A/m$^2$, the variation of $J_{\mathrm{m,PEM}}$ and $\eta_{\mathrm{a}}$ as a function of the PF loading is obtained. By varying the operating current density from 0 to 2000 A/m$^2$ and fixing the PF loading at a certain value, the anode polarization is calculated.

The cathode overpotential of the DMFC is also related to the PF loading in the anode CL because of the dependence of the methanol crossover on the PF loading in the anode CL. In addition, the cathode overpotential can be calculated using the following equation

$$i_{\mathrm{ct}} = i_{\mathrm{ref}}^{O_2} \left( \frac{c_{\mathrm{cc}}^{O_2}}{c_{\mathrm{ref}}^{O_2}} \right)^{\gamma_c} \exp\left( \frac{\alpha_{\mathrm{c}} F}{RT} \eta_{\mathrm{c}} \right) \tag{13}$$

where $i_{\mathrm{ct}} = i + 6FJ_{\mathrm{m,PEM}}$[23] is the total current density in the cathode CL.

Using the results for the anode, the variation of $i_{\mathrm{ct}}$ and $\eta_{\mathrm{c}}$ with the PF loading can be obtained. Similarly, the cathode polarization results can also be calculated.

The cell voltage of the DMFC is determined using the following equation

$$V = E_{\mathrm{cell}} - \eta_{\mathrm{a}} - \eta_{\mathrm{c}} - JR_{\mathrm{con}} - J \frac{\delta_{\mathrm{PEM}}}{\sigma_{\mathrm{PEM}}} \tag{14}$$

where $E_{\mathrm{cell}}$ is the electromotive force of DMFC, which can be calculated using $E_{\mathrm{cell}} = E_{\mathrm{cell}}^0 + (T - T_0) \frac{\partial E_{\mathrm{cell}}}{\partial T}$, and $E_{\mathrm{cell}}^0$ is the electromotive force under standard conditions. The variation of cell voltage with the PF loading and the polarization result can be obtained by combining the anode and cathode results.

In this section, relationships between anode/cathode overpotentials and PF loading were built using the methanol transfer parameters and the active surface area, which can be directly determined by adding PF, as intermediate parameters. After building these relationships, voltage-PF loading curves at a certain current density can be obtained as the ohmic polarization was assumed to be independent of the PF loading. Similarly, the voltage–current density curves (polarization curves) of the DMFCs can be obtained by setting the value of PF loading constant. The values for most of the parameters in the above analysis can be found in Table 1.

## Results and Discussion

### *Passive DMFC*

The addition of a PF in the anode CL of the DMFC enhances the active area for MOR due to the enlarged

**Table 1. Parameter Values**

| Parameter/Symbol (Unit) | Value |
|---|---|
| Cell temperature/T (K) | 298.15 |
| Reference methanol concentration/$c_{\mathrm{m}}^{\mathrm{ref}}$ (mol/m$^3$) | $1 \times 10^3$ |
| Reference oxygen concentration/$c_{\mathrm{ref}}^{\mathrm{O2}}$ (mol/m$^3$) | $1 \times 10^{-2} \times 101{,}325/(RT)$ |
| Diffusion coefficient of methanol in water/$D_{\mathrm{m,w}}$ (m$^2$/s) | $2.8 \times 10^{-9} \exp(\frac{2436}{353} - \frac{2436}{T})$ |
| Diffusion coefficient of methanol in membrane/$D_{\mathrm{m}}$ (m$^2$/s) | $4.9 \times 10^{-10} \exp(\frac{2436}{333} - \frac{2436}{T})$ |
| Faraday's constant/$F$ (A s/mol) | 96,487 |
| Standard reference exchange current density of the anode in absence of PF/$i_{\mathrm{ref,st}}$ (A/m$^3$) | 1100 |
| Reference exchange current density of the cathode/$i_{\mathrm{ref}}^{\mathrm{O2}}$ (A/m$^3$) | 1100 |
| Electro-osmotic drag coefficient of water in the PEM/$\lambda_{\mathrm{w}}$ | $2.9 \exp(\frac{1029}{333} - \frac{1029}{T})$ |
| Contact resistance of the fuel cell/$R_{\mathrm{con}}$ ($\Omega$ cm$^2$) | 1.2 |
| Conductivity of the Nafion membrane/$\sigma_{\mathrm{PEM}}$ (S/m) | $7.3 \exp(1268(\frac{1}{298} - \frac{1}{T}))$ |
| Transfer coefficient in the anode CL/$\alpha_{\mathrm{a}}$ | 0.5 |
| Transfer coefficient in the cathode CL/$\alpha_{\mathrm{c}}$ | 0.5 |
| Thickness of the anode DL/$\delta_{\mathrm{ad}}$ (m) | 0.0003 |
| Standard thickness of the anode CL in absence of PF/$\delta_{\mathrm{ac}}$ (m) | 0.00005 |
| Thickness of the cathode DL/$\delta_{\mathrm{cd}}$ (m) | 0.0003 |
| Thickness of the Nafion membrane/$\delta_{\mathrm{PEM}}$ (m) | 0.000175 |
| Density of the PF/$\rho_{\mathrm{PE}}$ (g/m$^3$) | 158,000 |
| Density of the water/$\rho_{\mathrm{w}}$ (g/m$^3$) | 100,000 |
| Standard active surface area of the anode CL in absence of PF/$a_{\mathrm{act,st}}$ (m$^2$/m$^2$) | 2100 |
| Standard porosity of the anode CL in absence of PF/$\varepsilon_{\mathrm{st}}$ | 0.3 |
| Standard volume of the anode CL in absence of PF/$V_{\mathrm{st}}$ (m$^3$) | $3 \times 10^{-5}$ |

porosity. The anode overpotential of the DMFC can, therefore, be reduced. However, this enlarged porosity can also increase the methanol crossover through the PEM because of the improved methanol transfer in the anode CL. In addition, the mixed potential in the cathode CL is increased. As a result, introduction of a PF into the anode CL of the DMFC during the MEA fabrication would significantly affect the cell performance in both the anode and cathode.

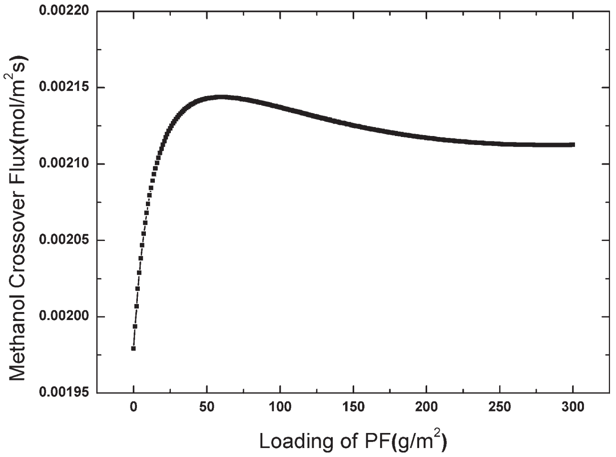

**Figure 2. Effect of the PF loading on the methanol crossover for a passive DMFC at a current density of 600 A/m$^2$.**

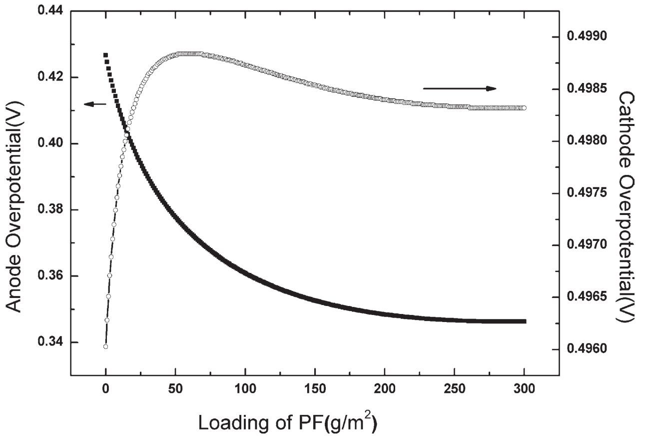

**Figure 3. Effect of the PF loading on the cathode and anode overpotentials for a passive DMFC at a current density of 600 A/m$^2$.**

Figure 2 demonstrates the variation of methanol crossover flux ($J_{\mathrm{m,PEM}}$) with the PF loading in the anode CL of a passive DMFC at a current density of 600 A/m$^2$, which can be directly calculated from Eq. 10. A methanol solution (3.0 mol/L) is used as fuel in the anode of the DMFC. It can be seen that the methanol crossover flux $J_{\mathrm{m,PEM}}$ increases steeply with the increasing PF loading at values below 30 g/m$^2$, and the total increase in $J_{\mathrm{m,PEM}}$ is approximately $1.5 \times 10^{-4}$ mol/m$^2$ s. This increase in methanol crossover with the PF loading results from the growing porosity of the anode CL. When the PF loading is greater than 50 g/m$^2$, $J_{\mathrm{m,PEM}}$ increases very slowly and finally becomes steady after the PF loading increases to the value of 250 g/m$^2$. An increase in the porosity can improve the methanol transfer in the anode CL and increase the methanol concentration at the anode CL/PEM interface, while the increase in CL thickness has the opposite effect. When the current density is constant, the PF loading in the anode CL can affect the cathode overpotential of the DMFC by altering the methanol crossover flux because the oxygen transfer behavior in the cathode cannot be influenced by the PF in the anode.

Figure 3 shows the dependences of the cathode and anode overpotential of the passive DMFC on the PF loading in the anode CL. These two overpotentials were obtained from Eqs. 7 and 13, respectively, by setting the current density constant. Compared with the cathode overpotential ($\eta_{\mathrm{c}}$), the anode overpotential ($\eta_{\mathrm{a}}$) is more strongly dependent on the PF loading at the operating current density of 600 A/m$^2$. $\eta_{\mathrm{a}}$ decreases rapidly as the PF loading increases from 0 up to 100 g/m$^2$. The decrease in $\eta_{\mathrm{a}}$ is approximately 66 mV by changing the PF loading in the anode CL from 0 to 100 g/m$^2$. For the same PF loading change, the increase in the cathode overpotential is only 3.0 mV, which is negligible compared with the decrease in $\eta_{\mathrm{a}}$. When the PF loading increases to over 100 g/m$^2$, $\eta_{\mathrm{a}}$ becomes steady in value.

By combining the effects of the PF loading on the anode and cathode overpotential, calculated variation of the cell voltage (Eq. 14) at 600 A/m$^2$ with the PF loading can be obtained as the solid line shown in Figure 4a. A gradual increase in the cell voltage is apparent as the PF loading increases. By increasing the PF loading from 0 to 100 g/m$^2$, the cell voltage is enhanced by approximately 63 mV. When the PF loading is higher than 100 g/m$^2$, the cell voltage becomes steady. By increasing PF loading from 100 to 300

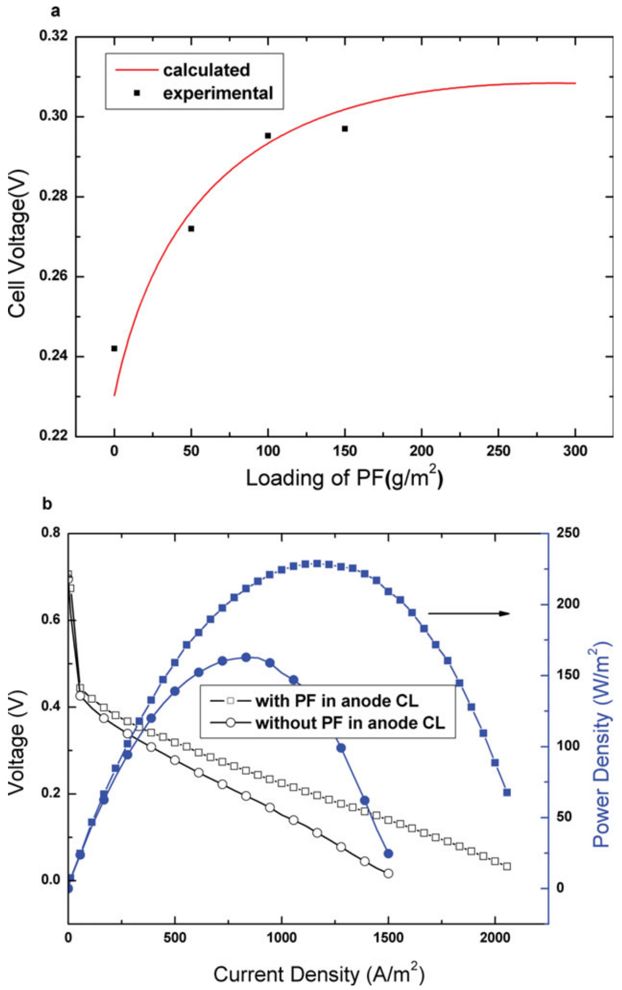

**Figure 4. (a) Effect of the PF loading on the cell voltage of a passive DMFC at 600 A/m$^2$ obtained by both calculation and experiments; (b) experimental polarization curves for the passive DMFC without and with PF (100 g/m$^2$) in the anode CL incorporated during the MEA fabrication (methanol concentration: 3.0 mol/L methanol solution).**

**[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

g/m$^2$, the cell voltage is enhanced by only 15 mV. These calculated results can be confirmed by the experimental results in the same figure. Experimentally, by incorporating 50 g/m$^2$ and 100 g/m$^2$ of PF into the anode CL during the MEA fabrication, the cell voltage of the passive DMFC increased from 0.242 V to 0.272 V and 0.295 V, respectively. When 150 g/m$^2$ PF was incorporated into the anode CL, the cell voltage of the DMFC was close to the value that was observed with 100 g/m$^2$ PF loading. It can be concluded that the addition of a PF into the anode CL can notably improve the performance of a passive DMFC, and the cell voltage may steadily increase with PF loading. When the PF loading reaches 100 g/m$^2$, changes in the cell voltage are not as substantial. Therefore, we consider 100 g/m$^2$ to be the optimal PF loading in the anode CL of a passive DMFC.

With the optimized PF loading in the anode CL, the experimental polarization curve of the passive DMFC with optimized PF loading was measured and shown in Figure 4b (3.0 mol/L methanol solution). For comparison, a conventional passive DMFC in the absence of PF in the anode CL was also fabricated and tested under the same conditions. It can be indicated that the maximum power density of the DMFC can be enhanced by approximately 37% using optimal PF loading in the anode CL.

### *Active DMFC*

The effect of PF loading in the anode CL on the performance of an active DMFC is also investigated. Figure 5a demonstrates the calculated relationship between the cell voltage of an active DMFC and the PF loading (Eq. 14). The current density is 600 A/m$^2$, and a 2.0 mol/L methanol solution is used as fuel in the anode. The cell voltage of the active DMFC varies in a manner similar to that of the passive DMFC (Figure 4a), and the cell voltage exhibits a 51 mV enhancement as a result of incorporating PF at 100 g/m$^2$ into the anode CL. When the PF loading is greater than 250 g/m$^2$, the cell voltage of the active DMFC becomes stable. Variations in the anode and cathode overpotentials with the PF loading (Eqs. 7 and 13) are shown in Figure 5b. The decreasing anode overpotential is the determining factor for the performance improvement of the active DMFC. $\eta_a$ decreases from 0.36 to 0.305 V. The increase in $\eta_c$ is only 3.0 mV, which is negligible.

For the active DMFC with optimized PF loading (100 g/m$^2$) in the anode CL, the anode and cathode polarization

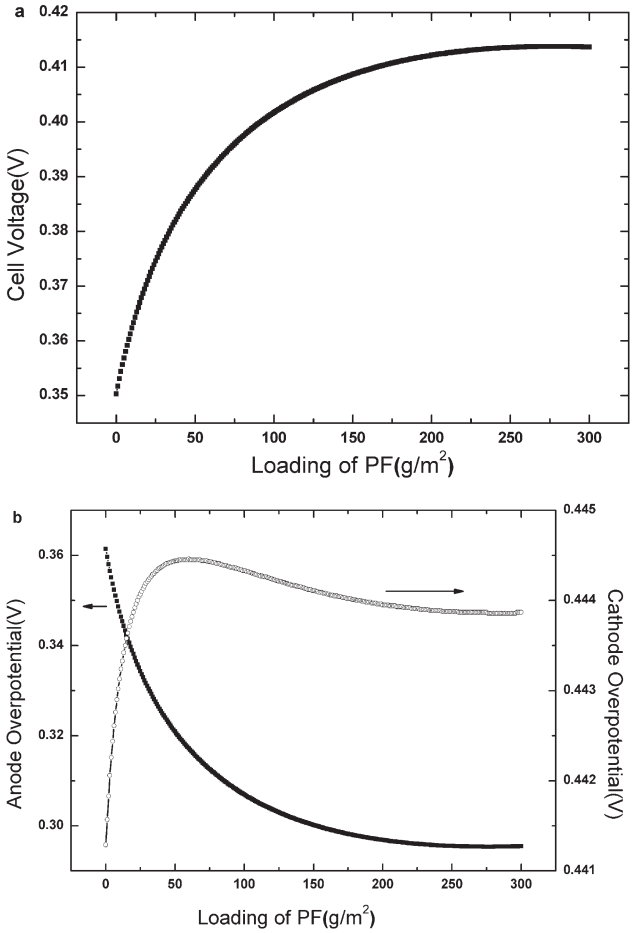

**Figure 5. Effect of the PF loading on the (a) cell voltage and (b) anode and cathode overpotentials of the active DMFC at a current density of 600 A/m$^2$.**

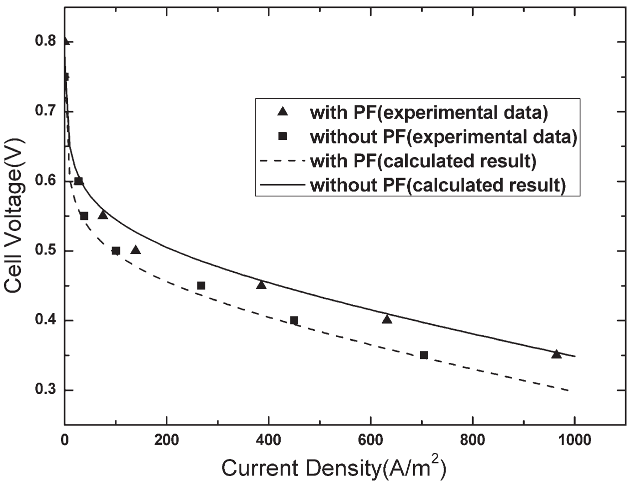

**Figure 6. Comparison between the experimental and calculated polarization data of an active DMFC with and without PF.**

results were, respectively, calculated from Eqs. 7 and 13 by setting the PF loading constant (100 g/m$^2$). With these results, the polarization curve of the active DMFC (solid line in Figure 6) can be obtained. For comparison, the polarization curve of the conventional DMFC (dashed line in Figure 6) was also calculated similarly by setting the PF loading in the anode CL at 0 g/m$^2$. Figure 6 also demonstrates the corresponding experimental data in previous study[24] for comparison. The catalyst loading in the anode and cathode CL (PtRu in the anode, Pt in the cathode) was 3.0 and 2.0 mg/cm$^2$, respectively. The calculated polarization results correlated well with the experimental data. Compared with the commonly fabricated DMFC (DMFC-C), the DMFC equipped with a PF in the anode CL (DMFC-P) has a lower open circuit voltage. This finding is due to the enhancement in methanol crossover flux that results from the greater porosity of the anode CL. The cell voltage of both DMFC-C and DMFC-P decreases sharply with increased current density after the current density exceeds zero because of the activation polarization in both the anode and the cathode. The DMFC-P performs better than the DMFC-C because of the lower anode overpotential that results from the higher active area for methanol electro-oxidation in the anode CL that is afforded by the PF.

It can be concluded that the PF addition in the anode CL can notably improve the cell performance of the active DMFC. The calculated cell voltage of the DMFC can be enhanced by approximately 15% at 600 A/m$^2$. A comparison between the calculated and experimental polarization results confirms that the DMFC-P performs better than the DMFC-C when the current density is greater than zero.

## Conclusions

This study successfully demonstrates the optimal loading of the PF to be incorporated into the anode CL of a DMFC using an empirical model. The effects of the PF loading in anode CL on the DMFC performance were investigated to design and optimize the microstructure of the anode CL. The optimal loading of the PF in the anode CL for both the passive and active DMFCs was calculated to be 100 g/m$^2$ with reference to the cell voltage. At an operation current density of 600 A/m$^2$, the cell voltage exhibited an enhancement of 63 and 51 mV for the passive DMFC and the active DMFC, respectively. The results calculated in this article can be used to guide practical applications of DMFC fabrication. According to the experimental results, the maximum power density of the passive DMFC exhibited a 37% increase at the optimal loading of PF in the anode CL. Calculated polarization results for the active DMFC also correlate well with the experimental results, which also confirms the validity of the empirical model. By modifying some parameters, the proposed model in this article can also be used for other fuel cells, such as proton-exchange membrane fuel cells (PEMFCs) and direct formic acid fuel cells.

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## Notation

$A_e$ = electrode area used in the model, m$^2$
$\alpha_a$ = transfer coefficient in the anode CL
$\alpha_c$ = transfer coefficient in the cathode CL
$\delta$ = thickness of a certain component, m
$\varepsilon_{\mathrm{ac}}$ = porosity of the anode CL with PF
$\varepsilon_{\mathrm{st}}$ = standard porosity of the anode CL in absence of PF
$\eta_a$ = anode overpotential, V
$\eta_c$ = cathode overpotential, V
$\kappa$ = contraction coefficient of the anode CL
$\lambda_w$ = electro-osmotic drag coefficient of water in the PEM
$\rho_{PF}$ = density of the PF, g/m$^3$
$\rho_w$ = density of water, g/m$^3$
$\sigma_{\mathrm{PEM}}$ = conductivity of the PEM, S/m
$a_{act}$ = active surface area for methanol oxidation in the anode CL, m$^2$/m$^2$
$a_{act,st}$ = standard active surface area of the anode CL in absence of PF, m$^2$/m$^2$
$c_m$ = methanol concentration, mol/m$^3$
$c_m^{ac}$ = methanol concentration in the anode CL, mol/m$^3$
$c_m^{ref}$ = reference methanol concentration in the anode CL, mol/m$^3$
$c_{cc}^{\mathrm{O2}}$ = oxygen concentration in the cathode CL, mol/m$^3$
$c_{\mathrm{ref}}^{\mathrm{O2}}$ = reference oxygen concentration in the cathode side, mol/m$^3$
$D_m$ = diffusion coefficient of methanol, m$^2$/s
$F$ = Faraday's constant, A s/mol
$i$ = operating current density of the DMFC, A/m$^2$
$i_a$ = surface current density in the anode, A/m$^2$
$i_{a,v}$ = volume current density in the anode, A/m$^3$
$i_{ct}$ = total current density in the cathode CL, A/m$^2$
$i_0$ = exchange current density in the anode CL, A/m$^3$
$i_{ref}$ = reference exchange current density in the anode CL, A/m$^3$
$i_{ref,st}$ = standard reference exchange current density of the anode in absence of PF, A/m$^3$
$i_{ref}^{\mathrm{O2}}$ = reference exchange current density in the cathode, A/m$^2$
$J_m$ = methanol flux, mol/m$^2$ s
$J_{m,PEM}$ = methanol crossover flux, mol/m$^2$ s
$M_w$ = molecular weight of water, g/mol
$R$ = universal gas constant
$R_{con}$ = contact resistance of the fuel cell, Ω cm$^2$
$s_{PF}$ = loading of PF in the anode CL, g/m$^2$
$T$ = cell temperature, K
$V_{st}$ = standard volume of the anode CL in absence of PF, m$^3$

### *Subscripts*

$ac$ = Anode CL
$ad$ = Anode DL
$ac-ad$ = Interface between the anode CL and DL
$ac-PEM$ = Interface between the anode CL and PEM
$ch$ = Anode flow channel
L = Liquid water
$PEM$ = Proton-exchange membrane

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