Addition of non-reacting gases to the anode flow field of DMFCs leading to improved performance

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Abstract

Contrary to conventional conceptions, we find that an external addition of non-reacting gases to the anode flow field of a direct methanol fuel cell led to improved cell performance. Our theoretical analysis shows that an increase in void fraction of the gas phase in flow channels reduces the cross sectional area of the liquid phase, thereby increasing the liquid velocity. The increased liquid velocity enhances the mass transfer of methanol from the flow channel to the gas diffusion layer and hence, improves cell performance. Following the same idea of accelerating the liquid velocity by reducing channel depth, we further demonstrate experimentally that thinning channel from 3.0 to 0.5 mm resulted in an increase in peak power density by 67.5%.

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1. Introduction

Direct methanol fuel cells (DMFC), using a solid polymer membrane as electrolyte and liquid methanol as fuel, have been projected as promising power sources for portable electronic devices, electric vehicles, and other applications, because, as compared with hydrogen-fed polymer electrolyte fuel cell (PEMFCs), they offer the basic advantages of a lower system volume and weight, a simpler system design, a simpler mode of operation with fast response and better dynamics as well as lower investment and operating costs [1–6]. The commercialization of DMFC is, however, still hindered by several technological problems, including a substantial methanol crossover through the polymer membrane, low electro-activity of methanol oxidation on anode, and severe cathode flooding. To circumvent these problems, much attention has been paid to modifying existing membranes and searching for alternatives [7–14], to evaluating and optimizing anode catalysts and structures [15–18], as well as to studying the effect of cathode on cell performance and performance stability of the DMFCs [19–23]. Relatively less effort, however, has been dedicated to optimizing the anode flow field of DMFCs [24–26]. In comparison with PEMFC, carbon dioxide is produced as a result of methanol electrochemical oxidation on anode of DMFCs. Therefore, gas management on anode is also an important issue in DMFC design. In line with this perspective, it has been thought that removing CO$_2$ from anode flow fields as efficiently as possible can free much more effective contact area, so that a continuous supply of liquid methanol from the anode flow field to the catalyst layer can create an improved cell performance [27–29]. Based on this conception, some investigators have been attempting to separate or remove CO$_2$ gas from anode flow channels [30–33]. Contrary to conventional thinking, however, in this work we injected CO$_2$ gas into methanol solution at the inlet of the anode flow field of a DMFC.
Surprisingly, we found this addition of the non-reacting gas led to substantial improvements in cell performance. In this work, we show that an external addition of gases increases the void fraction of the gas phase in flow channels, leading to a reduction in the cross sectional area of the liquid phase, which, in turn, causes an increase in the liquid phase flow velocity. The increased liquid velocity, in turn, enhances mass transfer of methanol from the flow channel to the gas diffusion layer and hence, improves the cell performance. We also demonstrate that for a given feeding mass flow rate of methanol solution, a reduction in channel depth also accelerates the liquid phase flow; and the cell test shows that thinner anode flow channels resulted in higher performance.

2. Experimental

2.1. Membrane-electrode assembly

A membrane-electrode assembly (MEA) having an active area of 4.0 × 4.0 cm² was fabricated in house employing two single-side ELAT electrodes from E-TEK and a Nafion® membrane 115. Both anode and cathode electrodes used carbon cloth (E-TEK, Type ‘A’) as the backing support layer with 30% PTFE wet-proofing treatment. The catalyst loading on the anode side was 4.0 mg cm⁻² with unsupported [Pt:Ru] Ox (1:1 a/o), while the catalyst loading on the cathode side was 2.0 mg cm⁻² using 40% Pt on Vulcan XC-72. Furthermore, 0.8 mg cm⁻² Nafion® was applied onto the surface of each electrode. Finally, the MEA was formed by hot pressing at 135 °C and 5 MPa for 3 min.

2.2. Single cell assembly and test loop

Together with gas sealing gaskets, the MEA was sandwiched between two bipolar plates and clamped using two transparent enclosures. The bipolar plates were made of 316 stainless steel, in which a single serpentine channel, 2.0 mm in channel width and 1.5 mm in rib width, was machined using wire-cut technology, resulting in a total channel length of 420 mm, and an open ratio of 52.8%. The experiments were carried out using the test loop detailed elsewhere [34,35]. Methanol solution was fed to the anode by a digital HPLC micro-pump (Series III), while oxygen flowing to the cathode was controlled and measured with a mass flow meter (Omega FMA-7105E) combined with a multiple channel indicator (Omega FMA-5876A).

In the experiments adding a non-reacting gas to the anode flow field, CO₂ gas was injected at the inlet of the anode flow channel and mixed with methanol solution. The CO₂ injection rate was varied and controlled by a rotameter (GIL-MONT GF-4542-1210).

\[ Q_{\text{in}} - Q_{\text{CH}_3\text{OH}_x} - Q_{\text{H}_2\text{O}_x} = A \cdot (1 - x_c) \cdot \frac{Q_{\text{CH}_3\text{OH}_x}}{A \cdot (1 - x_c)}, \]  

(1)

2.3. Electrochemical instrumentation and test conditions

An Arbin BT2000 electro-load interfaced to a computer was employed to control the cell operation condition and to measure the voltage-current (polarization) curve. Experiments were performed for the same cathode flow field under the conditions of 1 M methanol, 60 °C and dry oxygen at atmospheric pressure at a flow rate of 100 ml min⁻¹; effects of the CO₂ injection rate and anode channel depth were tested at different flow rates of methanol solution.

3. Results and discussion

Fig. 1 shows the effect of the CO₂ gas injection rate on the performance of the cell with the anode flow channel depth of 3.0 mm when methanol solution was fed at 0.5 ml min⁻¹. The CO₂ gas injection rate was varied from 0.0 (i.e., without gas injection), to 0.43, 0.95, 3.10 and 4.50 ml min⁻¹. Surprisingly, the addition of CO₂ gas at the flow rate of 0.43 ml min⁻¹ led to a substantial improvement in cell performance compared with that without gas injection; the maximum power density increased by 11.2%. This finding is contrary to the conventional design concept on CO₂ gas management that CO₂ should be removed as efficiently as possible from the anode flow field to increase the effective contact area between liquid fuel and the gas diffusion layer. Fig. 1 also shows, however, that too much gas injection (4.5 ml min⁻¹) resulted in a deterioration in cell performance, because the increased gas fraction caused the effective contact area between liquid fuel and the gas diffusion layer to be too small. In the following, we conduct an approximate analysis and show the mechanism leading to improved cell performance when an adequate amount of external non-reacting gases is added to the flow field.

Previous visual studies [34,35] indicated that under typical operating conditions, CO₂ gas bubbles and liquid methanol solution co-exist in the flow channel, but the void fraction of the gas phase, \( x_g \), increases with channel length. As an approximation, we divide the flow channel into two sub-regions: a divergent region occupied by the gas phase flow in the upper portion and a convergent region occupied by the liquid phase flow in the lower portion, as sketched in Fig. 2. Liquid methanol flow in the lower portion diffuses through the gas diffusion layer to catalyst sites, where it oxidizes, producing CO₂ gas. Based on the mass balance at a given cross section, the local liquid velocity along the flow channel can be approximated by
where $Q_{\text{in}}$ is the methanol solution flow rate at the inlet, $Q_{\text{CH}_3\text{OH},x}$ and $Q_{\text{H}_2\text{O},x}$ represent the consumption rates of methanol and water, respectively, and $A$ is cross-section area of the anode flow channel. Typically, the consumption rates of methanol and water are negligible as compared with the methanol solution flow rate even at higher current density; hence Eq. (1) can be simplified as:

$$u(x) = \frac{Q_{\text{in}}}{A \cdot (1 - x_{\alpha})}. \quad (2)$$

Eq. (2) indicates that either a reduction in channel cross-section area, $A$, or an increase in gas void fraction, $x_{\alpha}$, leads to a higher liquid velocity in the flow channel.

We now analyze mass transfer of methanol from the flow channel to the gas diffusion layer. As shown in Fig. 2, mass transfer equation in the liquid region can be written as:

$$u \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2}, \quad (3)$$

where $c$ is methanol concentration, and $D$ is mass diffusivity. The upper boundary is the liquid–gas interface ($y = H_{x}$), where liquid may evaporate but typically rather slowly; hence the upper boundary condition can be written as:

$$\frac{\partial c}{\partial y} \bigg|_{y = H_{x}} = 0, \quad (4)$$

and the lower boundary condition ($y = 0$) can be written as:

$$-D \frac{\partial c}{\partial y} \bigg|_{y = 0} = h_w \cdot (c_{\infty} - c_w), \quad (5)$$

where $h_w$ is the local mass transfer coefficient, and the term of $(c_{\infty} - c_w)$ represents the local difference of methanol concentration between the bulk liquid and the lower boundary ($y = 0$). With the introduction of non-dimensional variables:

$$U = \frac{u}{u_{\text{in}}}, \quad X = \frac{x}{L}, \quad Y = \frac{y}{L} \quad \text{and} \quad C = \frac{c}{c_{\infty} - c_w}. \quad (6)$$

Eq. (3) and the boundary conditions given by Eqs. (4) and (5) can be written in the dimensionless form as:

$$Pe_x \frac{\partial C}{\partial X} = \frac{\partial^2 C}{\partial Y^2} \quad (7)$$

and

$$\frac{\partial C}{\partial Y} \bigg|_{Y=H_x} = 0, \quad -\frac{\partial C}{\partial Y} \bigg|_{Y=0} = Sh_x, \quad (8)$$

where $Pe_x = (u \cdot L/D)$ is the local Peclet number, and $Sh_x = (h_x \cdot L/D)$ is the local Sherwood number. Integrating Eq. (7) from the lower boundary ($Y = 0$) to the upper boundary ($Y = H_x/L$) yields:
\[ Sh_x = \text{Pe}_x \cdot \int_0^\alpha \frac{\partial C}{\partial X} \, dY. \]  

Eq. (9) indicates that the mass transfer coefficient of methanol from the flow channel to the gas diffusion layer, represented by \( Sh_x \), increases with an increase in the local Peclet number, \( Pe_x \). For a given channel length, either an increase in the local liquid velocity or a decrease in channel cross sectional area results in an increase in \( Pe_x \). The addition of a gas to the flow channel causes the liquid velocity to increase (see Eq. (2)) and hence, enhances the mass transfer of methanol from the flow channel to the diffusion layer. This explains why the addition of a gas leads to improved cell performance, as shown in Fig. 1. An important implication of the effect of adding non-reacting gases in the anode flow field of a DMFC is that the \( CO_2 \) gas generated by electrochemical reaction in a DMFC cannot always be taken as a disadvantage. Instead, the presence of an adequate amount of \( CO_2 \) gas in the flow field enhances methanol mass transfer and thus may improve cell performance.

As indicated in Eq. (2), for the same flow rate, a reduction in the channel cross sectional area also leads
to a higher liquid velocity or higher $Pe_{eq}$, hence improving cell performance. A change in the channel cross sectional area, however, also causes a change in the open ratio of the bipolar plate, which is another important design parameter influencing cell performance. To keep the same open ratio, channel depth is the only parameter that can be changed to reduce the channel cross sectional area. We reduced channel depth from 3.0 to 2.0, 1.0 and 0.5 mm. The polarization curves corresponding to these channel depths are displayed in Figs. 3 and 4, corresponding, respectively, to 1.0 and 2.0 ml min$^{-1}$ in methanol solution flow rate. Both figures show clearly that for a given methanol solution flow rate, a decrease in the anode flow channel depth from 3.0 to 0.5 mm led to a significant improvement in cell performance; the maximum power density increased by 67.5% at 1.0 ml min$^{-1}$ and 64.4% at 2.0 ml min$^{-1}$. This experiment demonstrated that thinning flow channels, causing an increase in the liquid velocity, enhances mass transfer of methanol from the flow channel to the gas diffusion layer, leading to a higher cell performance. It must be pointed out, however, that a decrease in flow channel depth, (i.e., cross sectional area) leads to an increase in pressure drops over the flow channel, which increases the pumping power for the supply of methanol solution. As such, the overall efficiency of a DMFC system might decrease. Moreover, a higher pressure drop may force part of the methanol solution to flow directly through the diffusion layer without passing along the flow channel, leading to non-uniformly distribution of fuel over the entire MEA surface. However, the trade-off between the pros and cons caused by the change in channel depth and the optimization of an entire DMFC system will be investigated in the future work.

4. Conclusions

An external addition of CO$_2$ gas to the anode flow field of a DMFC leading to improved performance has been shown experimentally. This finding has been explained by a theoretical analysis into the anode flow field. It has been shown that an increase in void fraction of gas phase in the anode flow field reduces the cross sectional area of liquid phase, thereby increasing the liquid velocity. As a result of the increased liquid velocity, the mass transfer of methanol from the anode flow channel to the gas diffusion layer is enhanced, and an improved cell performance is achieved. This study also indicates that a decrease in the anode flow channel depth increases the liquid velocity. Following this idea, experiments have been performed to demonstrate a reduction in the anode flow channel depth from 3.0 to 0.5 mm, while keeping the same open ratio of the bipolar plate, resulting in an increase in peak power density by 67.5%.

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