Effect of anode backing layer on the cell performance of a direct methanol fuel cell

C. Xu, T.S. Zhao*, Q. Ye

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

Received 10 January 2006; received in revised form 15 February 2006; accepted 19 February 2006

Available online 11 April 2006

Abstract

We investigated experimentally the effect of the anode backing layers consisting of carbon papers with different thicknesses and different polytetrafluoroethylene (PTFE) contents on the cell performance of a direct methanol fuel cell (DMFC). The membrane electrode assemblies were prepared using the decal method such that the effect of different anode backing layers could be studied with the same anode catalyst layer, the same membrane and the same cathode. We found that a too thin anode backing layer resulted in lower cell voltages in the entire current density region, whereas a too thick backing layer led to a lower limiting current density. The reduced cell performance as a result of thinning the backing layer may be attributed mainly to the increased under-rib mass transport polarization as a result of weaker under-rib convection in a thinner backing layer. The experimental results also showed that the use of a PTFE-treated backing layer resulted in a lower limiting current density, attributing primarily to the increased mass transfer resistance as a result of the PTFE treatment.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Direct methanol fuel cells; Mass transfer; Diffusion layer; Wettability; Non-uniformity

1. Introduction

The liquid feed direct methanol fuel cell (DMFC), based on a polymer electrolyte membrane (PEM), has received much attention as a leading candidate power source for portable electronic devices, electric vehicles and other mobile applications, because of its unique advantages such as high energy-conversion efficiency, easy delivery and storage of liquid fuel, ambient temperature operation and simple construction [1–3]. The so-called diffusion layer (DL), one of the key components of a DMFC, usually consists of a backing layer, typically made of carbon paper or carbon cloth, and a coated thin micro-porous layer (MPL). The DL serves to uniformly distribute reactants over the electrode surface and electrically connect the catalyst layer (CL) and the current collector. Because of its unique importance in PEM-based fuel cells, the DL has been studied extensively [4–24]. Most of the previous studies on DLs have been focused on H2-fed PEMFCs to study the effects of MPL and the polytetrafluoroethylene (PTFE) content of the cathode backing layer on cell performance. Shukla and co-workers [4,5] investigated the morphology and hydrophobicity of the MPL on the performance of both a PEMFC and a DMFC. Bevers et al. [6] studied the properties of carbon papers with different PTFE contents, including through-plane conductivity, gas permeability and hydrophobicity. Lin and Nguyen [10] investigated the effect of thickness and wetproofing level of the DL on electrode flooding and cell performance of a H2-fed PEMFC, they reported that adding appropriate PTFE to the backing layer could enhance gas transport and alleviate water flooding of electrodes. Lim and Wang [11] studied the effect of hydrophobic polymer (i.e., FEP) content in the cathode DL on the cell performance of a H2-fed PEMFC. They found that 10 wt.% FEP loading was sufficient to result in a hydrophobic surface to facilitate liquid water removal, and higher FEP content in excess of 10 wt.% could only block the DL surface pores, thus imposing significant mass transport limitations due to both oxygen transport and water removal through a higher restricted DL surface.

In contrast, only a few papers have been reported to investigate the effect of the anode backing layer on the performance of DMFCs [13,15–17]. Perhaps borrowed directly from H2-fed PEMFC technology, heretofore, the DMFC anode backing layer has been usually PTFE-treated. In H2-fed PEMFCs, the use of
the PTFE-treated carbon paper as the cathode DL is to increase oxygen transport paths such that the limiting current density can be increased. At the anode of a liquid-fed DMFC, the counter gas–liquid two-phase flow usually occurs under normal operating conditions [3]. Both liquid phase transport paths and the counter gas phase transport paths have to be provided to reduce the polarization due to the DMFC anode mass transport. However, so far there has been no evidence showing whether the PTFE treatment of the DMFC anode backing layer is needed or not. If needed, it is still unclear how much PTFE should be coated in the backing layer. Argyropoulos et al. [16] found that Toray carbon paper was not a suitable anode backing material for DMFCs due to its poor gas removal properties, but their conclusion was only based on the comparison in cell performance between using carbon cloth and carbon paper both with high PTFE content. Scott et al. [15] and Oedegaard et al. [17] studied the effect of PTFE content in the carbon cloth of a DMFC, and they concluded that adding PTFE to the carbon cloth led to better gas transport. Liu et al. [18] adopted a sintered stainless steel fiber felt as the anode backing layer, and they found that hydrophilic backing layer might facilitate methanol transport and led to better cell performance.

The objective of this work is two-fold. First, we investigated experimentally the effect of thickness of the anode backing layer on the cell performance of a DMFC. The second objective of this work was to investigate the effect of PTFE content in the anode backing layer on the DMFC cell performance. Particularly, in terms of its effect on mass transport of reactants and on cell performance, we intended to clarify the necessity of PTFE-treating the DMFC anode backing layer. To accomplish these two objectives, it is essentially to ensure that the change in cell performance is solely caused by the change in the anode backing layer, rather than the effects from other components of the DMFC. To this end, we employed the decal method for fabricating membrane electrode assemblies (MEA) such that the effect of different anode backing layers could be studied for the same anode catalyst layer, the same membrane and the same cathode.

2. Experimental

2.1. Anode backing layer

Toray carbon papers from E-TEK with different thicknesses, as listed in Table 1, were used as the anode backing layer. As seen from Table 1, the first four samples were plain carbon papers and had zero PTFE content, whereas the others were wetproofed by the following procedures. The carbon papers were dipped entirely in 5.0 wt.% PTFE-emulsion (Du Pont) for 60 s and dried at room temperature. Repeat this step until the desired PTFE content was coated on the carbon papers. After that, the samples were sintered in air at 290 and 350 °C each for half an hour. The amount of PTFE and the calculated porosity of the treated samples were also shown in Table 1. PTFE wt.% was calculated as the weight ratio of PTFE to carbon paper. The morphology of thus obtained carbon papers was examined by a scanning electron microscope (SEM, JEM-6300).

Fig. 1. Schematic of the MEA fabricated with the decal method at the DMFC anode.

2.2. Membrane electrode assembly

The MEA having an active area of 3.0 cm × 3.0 cm was fabricated in-house employing a Nafion 115 membrane and two electrodes. The cathode electrode was a single-side ELAT electrode from E-TEK, which used carbon cloth (E-TEK, type A) as the backing layer with 30 wt.% PTFE wetproofing treatment. The catalyst loading on the cathode was 2.0 mg cm−2 using 40% Pt on Vulcan XC-72. On the anode, the catalyst layer was fabricated in-house by the decal method [25]. Catalyst ink was prepared using the reported method [25] and sprayed onto the Teflon blank. The catalyst layer was then transferred onto the membrane by hot pressing the catalyst coated Teflon blank and the cathode electrode on the two sides of the membrane at 135 °C and 4.0 MPa for 3 min, as depicted in Fig. 1. The anode catalyst loading was about 3.7 mg cm−2 using unsupported Pt–Ru black (atomic ratio Pt:Ru = 1:1, E-TEK). Carbon papers with different thicknesses and different PTFE contents were used to put on the anode catalyst layer as the anode diffusion media. The decal method described above ensures that the effect of anode backing layer be investigated using different carbon papers for the same anode catalyst layer, the same membrane and the same cathode.

2.3. Single cell assembly and the test rig

The MEA was sandwiched between two fixture plates. For convenience of temperature control, both the anode and cathode fixture plates were made of aluminum blocks. Both the anode and the cathode flow fields (which also served as current collectors) were made of 316L stainless steel. Single serpentine flow fields, having 1.0 mm channel width, 1.0 mm rib width and 1.0 mm depth, were formed on both the anode and cathode sides by wire-cut technique. To reduce the electrical resistance, the flow fields were sputtered with a thin layer of Pt (0.2 μm). It should be pointed out that carbon papers are fragile and prone to be crushed by collector ribs when gasket thickness is unmatched or the compressing pressure is too high [13]. Consequently, carbon paper crushing would increase significantly the methanol
Properties of the carbon papers tested

<table>
<thead>
<tr>
<th>Diffusion media</th>
<th>Thickness (mm)</th>
<th>Gasket thickness (mm)</th>
<th>PTFE content (wt.%)</th>
<th>Porosity a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon paper Toray-030</td>
<td>0.09</td>
<td>0.11</td>
<td>0</td>
<td>0.728</td>
</tr>
<tr>
<td>Carbon paper Toray-060</td>
<td>0.17</td>
<td>0.17</td>
<td>0</td>
<td>0.728</td>
</tr>
<tr>
<td>Carbon paper Toray-090</td>
<td>0.26</td>
<td>0.26</td>
<td>0</td>
<td>0.728</td>
</tr>
<tr>
<td>Carbon paper Toray-120</td>
<td>0.35</td>
<td>0.33</td>
<td>0</td>
<td>0.728</td>
</tr>
<tr>
<td>Carbon paper Toray-090</td>
<td>0.26</td>
<td>0.26</td>
<td>3.8</td>
<td>0.720</td>
</tr>
<tr>
<td>Carbon paper Toray-090</td>
<td>0.26</td>
<td>0.26</td>
<td>8.0</td>
<td>0.710</td>
</tr>
<tr>
<td>Carbon paper Toray-090</td>
<td>0.26</td>
<td>0.26</td>
<td>11.7</td>
<td>0.702</td>
</tr>
<tr>
<td>Carbon paper Toray-090</td>
<td>0.26</td>
<td>0.26</td>
<td>16.5</td>
<td>0.690</td>
</tr>
</tbody>
</table>

* Calculated by assuming the density of PTFE is 2.15 g cm⁻³, the density of carbon paper is 0.49 g cm⁻³, the thickness of Toray-090 is 0.26 mm, and the porosity of non-wetproofing paper is 0.728.

Transfer resistance, deteriorating cell performance. To avoid carbon paper crushing, special caution had to be taken to select appropriate gasket thickness for each carbon paper. Table 1 lists the gasket thickness corresponding to each tested carbon paper.

The experiments were carried out in the test rig detailed elsewhere [3]. On the anode, aqueous methanol solution was fed by a digital HPLC micro-pump (Series III). Before entering the cell, methanol solution was pre-heated to a desired temperature by a heater connected to a temperature controller. On the cathode, 99.999% high purity oxygen was supplied without humidification. A mass flow meter (Omega FMA-7105E), along with a multiple channel indicator (Omega FMA-5876A), was used to control and measure the flow rate of oxygen.

Fig. 2. Polarization curves for the anode backing layer consisting of carbon papers with different thicknesses (methanol solution feed flow rate: 1.0 ml min⁻¹; temperature: 75 °C): (a) 1.0 M, (b) 2.0 M and (c) 4.0 M.
2.4. Measurement instrumentation and test conditions

In this work, the Arbin BT2000 (Arbin Instrument) electro-load interfaced with a computer was employed to control the cell operation and measure voltage–current (polarization) curves. All the experiments were performed at temperature of 75 °C and fed with a constant oxygen gas flow rate of 200.0 standard cubic centimeters per minute (SCCM) at atmospheric pressure. Methanol concentration was varied from 1.0 to 4.0 M, while the flow rate was fixed at 1.0 ml min⁻¹.

3. Results and discussion

3.1. Effect of thickness of the anode backing layer

Fig. 2 shows the polarization curves of the DMFC with the anode backing layer consisting of each of the first four carbon papers listed in Table 1, which were not wetproofed but had different thicknesses. The experiments were performed at 75 °C and at the same flow rate of 1.0 ml min⁻¹ but different methanol concentrations. For lower methanol concentration of 1.0 M, Fig. 2a indicates that different anode backing layer thicknesses resulted in different voltages. The thinnest carbon paper (Toray-030) yielded the lowest cell voltage nearly in the whole current density region. With the increase in carbon paper thickness (i.e., Toray-060 and Toray-090), the cell voltage increased, and the carbon paper with the medium thickness (Toray-090) gave the highest voltage in the entire current density region. However, with a further increase in carbon paper thickness (Toray-120), the cell voltage remained almost the same as that for Toray-090 in the low current density region (<200 mA cm⁻²), while dropped rapidly with increasing current density. Therefore, there exists an optimal carbon paper thickness that results in the best cell performance. The change in carbon paper thickness can lead to two consequences: one is the change in the internal electrical resistance and the other is the change in the mass transfer resistance. Therefore, the cell performance behavior presented in Fig. 2a can be explained in terms of the change in these two parameters.

The internal electrical resistance of the MEA is supposed to increase with carbon paper thickness. However, our measurements showed that the internal electrical resistances of the MEAs with the first four carbon paper samples were almost the same (about 156 mΩ cm² ± 1.5%), indicating that the increased electrical resistance caused by the thicker carbon paper was negligibly small. This is because that the internal electrical resistance of a MEA predominately depends on the resistance of the membrane. This fact suggests that the change in cell performance presented in Fig. 2a be not caused by the internal electrical resistance, but solely by the changes in the mass transfer resistance, which is elaborated as follows.

The mass transport of methanol at the anode of the fuel cell can be described by referring Fig. 3, which depicts the paths for methanol solution to be transported from flow channel to the catalyst layer. Owing to the presence of channel ribs, the mass transport process can be divided into two regions: the channel region and the rib region. In the channel region, methanol solution is transported to the catalyst layer, primarily through a route normal to the plane (referred to as through-plane) by both convection and diffusion, due to the pressure difference and concentration difference between the flow channel and the catalyst layer. In the rib region, because of the effect of channel rib, the mass transport route becomes much more complex. In addition to diffusion, under-rib convection induced by the pressure difference between two adjacent serpentine flow channels (P_high − P_low) may be the predominated mass transport mechanism in the rib region. The mass transfer rate of methanol under ribs depends on the local flow rate of methanol solution (referred to as the under-rib flow rate). The under-rib flow rate depends on the pressure difference (P_high − P_low), the permeability of the backing layer, and the cross-sectional area of the flow stream (or the thickness of the backing layer). For the same pressure difference (P_high − P_low) (depending upon the methanol solution feed flow rate in the flow channel) and the same permeability of the backing layer, the under-rib flow rate increases with thickening the backing layer. Therefore, the under-rib convection effect becomes more significant with increasing the backing layer. When the backing layer is too thin, e.g., using the carbon paper Toray-030, the under-rib convection will become extremely weak, resulting in a larger concentration loss (or larger mass transport polarization) under ribs. This explains why the thinnest carbon paper (Toray-030) exhibited the lowest voltages in the entire current density region, as shown in Fig. 2a. As the backing layer becomes thicker, the effect of under-rib convection becomes stronger, increasing the methanol concentration under ribs. This is why the thicker carbon papers (Toray-060 and -090) yielded higher voltages than did the thinnest carbon paper (Toray-030). On the other hand, however, the through-plane mass transfer resistance increases with thickening the backing layer. As a result, for the fixed feed methanol concentration, thicker carbon papers will lead to lower methanol concentration in the channel region, although the difference in methanol concentration between the rib and channel regions is small due to the stronger effect of under-rib convection. This explains why the cell performance became worse when the carbon paper Toray-090 was changed.
It is interesting to see from Fig. 2a that the thickest carbon paper yielded the smallest limitation current density, as its through-plane mass transfer resistance was too large. In summary, the best cell performance of Toray-090 both in the low current density region and in the mass transport polarization region resulted from the excellent under-rib convection and reasonable through-plane diffusion. It is worth mentioning that the rates of methanol crossover for different carbon paper thicknesses may be different due to the change in the mass transfer resistance through the DL, which may also influence the cell performance. However, it can be seen from Fig. 2 that for a fixed methanol concentration the cell voltages at rather low current densities (less than 50 mA cm\(^{-2}\)) are nearly the same for different carbon paper thicknesses, meaning that the effect of carbon paper thickness on the rate of methanol crossover was negligibly small in this work. This may be due to the fact that the mass transfer resistance of methanol permeation through the membrane (Nafion 115) is much larger than that in the diffusion layer. As a result, the rates of methanol crossover for all the carbon papers tested with the same methanol concentration are almost the same.

![Fig. 4. Maximum power density vs. methanol concentration for the anode backing layer consisting of carbon papers with different thicknesses (methanol solution feed flow rate: 1.0 ml min\(^{-1}\); temperature: 75 °C).](image)

![Fig. 5. Polarization curves for the anode backing layer consisting of the carbon paper (Toray-090) with different PTFE contents (methanol solution feed flow rate: 1.0 ml min\(^{-1}\); temperature: 75 °C): (a) 1.0 M, (b) 2.0 M and (c) 4.0 M.](image)
When methanol concentration was increased to 2.0 and 4.0 M, the polarization curves for all the carbon papers with different thicknesses presented in Fig. 2b and c indicate that the cell voltage corresponding to each carbon paper drops toward zero with no occurrence of the limiting current density. This observation seemingly suggests that the mass transport of methanol is not a problem with a higher methanol concentration operation. However, it is clearly noticed from Fig. 2b and c, thickness of carbon paper still makes substantial difference in the polarization curves with increasing current density. This difference in cell performance between thinner and thicker carbon papers is related to the effect of under-rib convection. With the thinnest carbon paper (Toray-030), although the methanol concentration in the channel region is sufficiently high, the methanol concentration in the rib region may be still low due to the weakest effect of under-rib convection. With increasing the carbon paper thickness, the effect of under-rib convection becomes stronger, leading to more uniform methanol distribution and thereby improving the cell performance.

Fig. 4 presents the maximum power density, \( P_{\text{max}} \), versus the concentration of methanol solution for the different carbon papers. Toray-090 gave the highest \( P_{\text{max}} \) for all the methanol concentrations, indciting that this carbon paper has the optimal thickness for cell performance under the conditions tested in this work. It is also seen from Fig. 4 that the thinnest carbon paper yielded the lowest \( P_{\text{max}} \), regardless of methanol concentrations. In summary, the backing layer should not be too thin to avoid the non-uniform methanol distribution owing to the presence of channel ribs. With increasing the carbon paper thickness, the increased effect of under-rib convection tends to result in a more uniform methanol distribution, thereby improving the cell performance.

3.2. Effect of PTFE content

Fig. 5 shows the polarization curves of the DMFC with carbon paper Toray-090 having different PTFE contents as the anode backing layer, i.e., the last four samples listed in Table 1. The experiments were performed at 75 °C and at the same flow rate of 1.0 ml min\(^{-1}\) but different methanol concentrations. For low methanol concentration of 1.0 M, Fig. 5a shows that different PTFE contents yielded almost the identical voltage in the low current density region (<200.0 mA cm\(^{-2}\)). However, with increasing current density, the polarization curves for the backing layer with different PTFE contents became increasingly divergent, eventually reaching the corresponding limiting current density. It is evident from Fig. 5a that the limiting current density decreased step by step with increasing PTFE content. When the PTFE content was changed from 0 to 16.6 wt.%, the limiting current density was decreased from about 715.0 to 392.0 mA cm\(^{-2}\). It is understood that the limiting current density is inverse proportional to the mass transfer resistance of methanol from flow channel to DL [26], i.e.,

\[
\lim \frac{\text{current density}}{1} \text{for different methanol concentrations.}
\]

\[
\lim \frac{\text{current density}}{1} \text{for different methanol concentrations.}
\]

where \( h_{\text{lim}} \) is the limiting current density, \( F \) the Faraday constant, \( C \) the averaged methanol concentration in the channel and \( k_{\text{eff}} \) is the overall mass transfer coefficient from channel to the DL, indicating the reciprocal of mass transfer resistance. Eq. (1) indicates that the decrease in the limitation current density is due to the decrease in the mass transfer coefficient, or the increased mass transfer resistance as a result of increasing PTFE content. Before explaining why the PTFE treatment will result in an increase in the mass transfer resistance, let us look at the cell performance with higher methanol concentrations of 2.0 and 4.0 M shown in Fig. 5b and c. As seen from Fig. 5b, the performance difference due to the mass transfer polarization for the distinct PTFE contents became rather smaller at 2.0 M, and the difference was negligibly smaller at 4.0 M, as evident from Fig. 5c. The results presented in Fig. 5c indicate that a sufficiently higher methanol concentration would compensate the increased mass transfer resistance as a result of the PTFE treatment. The maximum power density, \( P_{\text{max}} \), versus the concentration of methanol solution for the different PTFE contents is shown in Fig. 6. It is clear that the increased mass transfer resistance resulting from the PTFE treatment degraded the maximum power density largely at low methanol concentration, but at high methanol concentration the maximum power density was almost the same regardless of the PTFE contents. In particular, Fig. 6 shows that the non-wetproofed carbon paper always has the highest maximum power density for different methanol concentrations.

The increased mass transfer resistance of methanol as a result of the PTFE treatment can be attributed to the following two reasons. First, the PTFE treatment will change the wettability of the carbon paper and make it more hydrophobic. It is understood that as the PTFE content increases, the contact angle of the carbon paper increases, providing more paths for gas flow [6,20]. However, the increased gas flow paths as a result of increasing PTFE content will also cause the liquid transport paths to decrease, indicating that the liquid saturation in the carbon paper may diminish greatly with the increase of PTFE content. As a
The effective diffusivity and the relative permeability of liquid phase will be reduced, both of which increase the mass transfer resistance due to diffusion and convection. In summary, increasing PTFE content in the carbon paper will make the gas transport faster but make liquid transport slower.

The second reason responsible for the increased mass transfer resistance as a result of the PTFE treatment is related to the changed pore morphology of the carbon paper [6,11]. Fig. 7 shows the morphology of the carbon paper with different PTFE contents. For the non-wetproofed carbon paper, as shown in Fig. 7a, the open pores were nearly uniformly distributed, and very little carbon film appeared near the fiber connections resulting from the carbon paper fabrication process [7]. However, with the increase of PTFE content, more thin film occurred and more open pores were blocked by PTFE thin film. As can be seen from Fig. 7c, over half pores were blocked by the film when the PTFE content reached 16.5 wt.%, although the overall porosity underwent a rather small change after PTFE treatment (less 5.0%, as shown in Table 1) [19]. This film-shaped PTFE in the carbon paper may significantly reduce the permeability of the carbon paper and thus resisted the methanol transfer from the channel to the CL. Therefore, from the viewpoint of enhancing mass transport of methanol solution to reduce the mass transport polarization, a carbon paper without PTFE treatment is preferred to be the anode backing layer of a DMFC.

4. Concluding remarks

To gain a better understanding of the effect of the anode backing layer on the DMFC performance, we tested eight anode backing layers consisting of carbon papers with different thicknesses and different PTFE contents for the same anode catalyst layer, the same membrane and the same cathode. The experimental results have shown that when a too thin carbon paper was used as the anode backing layer, the voltages generated by the fuel cell were low in the entire current density region. On the other hand, when a too thick carbon paper was used, the fuel cell yielded a low limiting current density. The reduced cell performance as a result of thinning the backing layer may be attributed mainly to the increased under-rib mass transport polarization as a result of weaker under-rib convection in a thinner backing layer. The reduced limiting current density associated with the thicker backing layer was due to the increased through-plane mass transfer resistance. It must be pointed out that although a higher methanol concentration can compensate the mass transport polarization due to the increased through-plane mass transfer resistance, an increase in methanol concentration cannot substantially change the non-uniform distribution of methanol due to the presence of channel ribs. The experimental results also showed that the use of a PTFE-treated backing layer resulted in a lower limiting current density, due to the increased mass transfer resistance possibly caused by the reduced wettability and decreased permeability of the PTFE-treated carbon paper. Therefore, from the viewpoint of enhancing mass transport of methanol solution to reduce the mass transport polarization, the anode backing layer of a DMFC does not need to be treated with PTFE.
Acknowledgement

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKUST6197/03E).

References