A crack-free and super-hydrophobic cathode micro-porous layer for direct methanol fuel cells

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HIGHLIGHTS

- A crack-free and super-hydrophobic cathode MPL is proposed.
- The new MPL enables a significant increase in the water recovery flux.
- The use of the new MPL improves the power density by more than 30%.

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ABSTRACT

A critical issue in operating passive direct methanol fuel cells (DMFCs) with neat methanol is finding a way to passively transport water generated at the cathode to the anode through membranes. This is so that the water required for anodic methanol oxidation can be compensated. The corresponding water flux depends on the capillary pressure created by the cathode micro-porous layer (MPL). Conventional MPLs made of carbon powder suffer from the problem of mud-cracks, significantly reducing the capillary pressure. In this work, we propose a cathode MPL prepared with fluorinated carbon nanotubes. It is demonstrated that the fluorinated nanotube MPL has no mud-cracks and its contact angle is as high as 153°. The application of the crack-free and super-hydrophobic MPL to a passive DMFC operating with neat methanol enables a significant increase in the water recovery flux, improving the anodic methanol oxidation reaction and thereby boosting the cell performance.

1. Introduction

Passive DMFCs have attracted much attention as a Prosing power source for portable electronic devices [1–6], due to its attractive features, including low-operating temperature, compact structure, convenience in fuel storage, and high theoretical energy density. However, methanol crossover, which means that methanol permeates from the anode to the cathode through proton exchange membranes, is still a technical issue impeding the commercialization of DMFCs. Therefore, to minimize the influence of methanol crossover, methanol solutions with low concentrations, typically from 2.0 M to 6.0 M, are usually applied in passive DMFCs. Although the impact of the methanol crossover has been alleviated with the diluted fuel, the original advantage of high energy density is dramatically sacrificed.

To ensure that the energy density of DMFCs is high enough for portable devices, concentrated methanol, especially neat methanol, are required to be fed. For this reason, vapor-feed fuel supply was proposed, which helps to achieve the neat methanol operation and meanwhile control the rate of methanol crossover [7–9]. Water management is extremely important for vapor-feed DMFCs, since no water is supplied from the anode fuel tank, water produced at the cathode must be passively transported to the anode to supply the required water for the anodic methanol oxidation reaction (MOR) [10–14]. Masdar et al. [10] investigated the effect of air filter on water management; it has been proved that the adoption of air filter can retard the water loss and further enhance water recovery. Li and Faghri [11] proposed a method to enhance the water recovery by controlling the cathode open ratios and showed that an optimal cathode open ratio could achieve both the small water loss and sufficient oxygen supply. Xu et al. [12] tested different approaches, including utilizing a thinner membrane, adopting a water management layer or an air filter to improve the water management. Their results indicated that by adopting a water management layer, an air filter layer, or a thinner membrane, the water management will be improved, not only increasing the water recovery, but also suppressing the methanol...
crossover. Wu et al. [13] proposed a thin layer consisting of Nafion ionomer and hygroscopic SiO2 nanoparticles that was coated onto the proton exchange membrane to achieve better water management. Due to the hygroscopic feature of SiO2, the thin layer at the cathode side can help to maintain the produced water at a higher concentration to increase the water back transport, and the thin layer at the anode side can retain more water which is from the cathode. Wu et al. [14] also proposed another innovative approach, a sandwich structure membrane consisting of an ultra-thin catalyst layer located between two thin membranes, to enhance the water recovery. The permeated methanol and the permeated oxygen meet and react in the membrane to generate water and carbon dioxide; the created water source can supply the water required for the MOR.

The previous efforts did achieve better water management. However, the previous approaches changed the original structure of DMFCs and markedly increased the system complexity. It is well known that the cathode micro-porous layer plays an important role in influencing the water transport behavior. For this reason, we propose a crack-free and super-hydrophobic MPL to improve water management. Carbon nanotubes were adopted and fluorinated to solve the issue of mud-cracks and to achieve a super-hydrophobic MPL. The results show that the application of the crack-free and super-hydrophobic MPL to a passive DMFC operating with neat methanol enables a significant increase in the water recovery flux, improving the anodic MOR and thereby boosting the cell performance.

2. Analysis

In the initial operation of a DMFC system with neat methanol, there is no water at the anode, while water is generated at the cathode. It follows that a water concentration gradient through the membrane is created, leading to a water diffusion flux:

\[ J_d = D_{\text{eff}} \frac{C_{\text{ic}} - C_{\text{ia}}}{d_m} \]  \hspace{1cm} (1)

where \( D_{\text{eff}} \) is the effective diffusivity of water in the membrane, \( d_m \) is the thickness of membrane, \( C_{\text{ic}} \) and \( C_{\text{ia}} \) represent the water concentrations at the cathode and anode surfaces facing to the membrane respectively.

Meanwhile, the liquid pressure as a consequence of the water generation at the cathode CL is gradually built up, leading to a convection flux driven by the liquid pressure difference through the membrane:

\[ J_c = \frac{K_m p_c - p_a}{\mu M_{\text{H}_2\text{O}} d_m} \]  \hspace{1cm} (2)

where \( K_m \) is the permeability of the membrane, \( \rho \) is the water density, \( \mu \) is viscosity of liquid water, \( M_{\text{H}_2\text{O}} \) is molecular weight of water, \( p_c \) and \( p_a \) represent, respectively, the liquid pressures at the cathode and anode CLs. Since there are both liquid and vapor phases at the anode CL and the liquid saturation is rather low, the liquid pressure is almost the same as the gas pressure at the anode [15]. At the cathode, the difference between the pressures of gas and liquid phase is related to the capillary pressure created by the cathode MPL, which is given by:

\[ p_c = p_{gc} - p_{kc} = \sigma \cos \theta \left( \frac{E}{K} \right)^{1/2} J(s) \]  \hspace{1cm} (3)

where \( p_{gc} \) is the cathode gas pressure, \( \sigma \) is the surface tension, \( \theta \) is the contact angle between the water and the surface of MPL, \( E \) and \( K \) are, respectively, the porosity and permeability of MPL, and \( J(s) \) is the Leverett function.

For passive vapor-feed DMFCs, the gas pressures at both electrode sides equal to the atmospheric pressure, thus the convection flux can be obtained as:

\[ J_c = \frac{K_m \rho \sigma \cos \theta}{\mu M_{\text{H}_2\text{O}} d_m} \]  \hspace{1cm} (4)

Hence, with a hydrophobic cathode MPL (\( \cos \theta < 0 \)), the convection flux is from the cathode to the anode.

In addition, another contribution to water crossover is the electro-osmotic drag by proton transport from the anode to cathode. The corresponding flux is given by:

\[ J_{eo} = n_d \frac{i}{F} \]  \hspace{1cm} (5)
with \( n_d \), \( i \) and \( F \) standing for the electro-osmotic drag coefficient in the membrane, current density and Faraday’s constant, respectively.

Therefore, the net water back flux can be obtained from Eqs. (1), (4) and (5) as:

\[
J_w = J_d + J_c - J_{eo} = D_{eff} \frac{C_e - C_l}{\delta_m} - \frac{K_m \rho \sigma \cos \theta}{\mu M_{H_2O} \delta_m} \left( \frac{P}{K} \right)^{1/2} J(s) - n_d \frac{i}{F} \quad (6)
\]

To compensate the water required for anodic MOR, a sufficiently large water recovery flux should be achieved. As indicated in Eq. (6), a larger water recovery flux can be obtained by increasing the capillary pressure created by the cathode MPL, which is determined by both the hydrophobicity (\( \theta \)) and the permeability (\( K \)).

3. Experimental

3.1. Carbon materials and the fluorination of carbon nanotubes

To prepare the cathode micro-porous layer, commercialized carbon powder (Vulcan XC-72R), multi-walled carbon nanotube (MWCNT) and hydroxylic MWCNT were used. The process of the chemical modification of hydroxylic MWCNTs to fluorinate MWCNTs is shown in Fig. 1. The hydroxylic MWCNTs were fluorinated by refluxing in the solution of dodecafluorohexylpropyl-trimethoxysilane (C\(_{13}\)H\(_{18}\)F\(_{12}\)O\(_3\)Si) 20 vol% in ethanol solvent at 50 °C for 50 h. The fluorinated MWCNTs were filtered and washed with deionized water repeatedly, then were dried overnight at 70 °C under vacuum.

3.2. MEA preparation

A Nafion® 212 membrane and a commercially available anode electrode from Johnson Matthey® were adopted in this work. At the cathode, using the catalyst-coated membrane (CCM) method the CL was fabricated in-house and directly coated onto the membrane: carbon supported Pt (60% Pt) from Johnson Matthey® was used as the catalyst with a loading of 2.0 mg cm\(^{-2}\) and the content of Nafion ionomer was 20 wt.%. These components were assembled by hot-pressing at 135 °C and 4.0 MPa for 3 min. The cathode CL
was directly coated onto the membrane to ensure the effect of different MPLs be investigated under the same condition, using the same anode, the same membrane and the same cathode CL. The active area of the MEA was 4.0 cm$^2$.

At the cathode DL, a Toray-060 carbon paper with 20 wt.% PTFE wet-proofing treatment worked as a backing layer. Different carbon materials, including XC-72R, MWCNT, hydroxylic MWCNT and fluorinated MWCNT, and PTFE were used to form the cathode MPL, and the content of PTFE and carbon loading were maintained 30 wt.% and 3.0 mg cm$^{-2}$.

The cathode MPLs were characterized by a contact angle measurement system, scanning electron microscope (JEOL-6390) and energy dispersive X-ray spectrum.

3.3. Single cell structure

The MEA was placed between an anode and a cathode perforated current collector. And the setup was sandwiched by the anode and the cathode fixture, a 5 mL fuel tank was constructed at the anode. Different from conventional passive DMFC structure, a gas gap with a thickness of 10 mm, a perforated plate with an open ratio of 15% and a 28 μm pervaporation membrane were employed at the anode to realize the neat methanol operation. A reversible hydrogen electrode was installed as reference electrode to measure the anode and the cathode potentials respectively. The schematic of the system is shown in Fig. 2. More details of the system structure can be found elsewhere [14,16].

3.4. Measurement instrumentation and test conditions

An Arbin BT2000 electrical load was used to control the discharging condition and record the data. For each discharging current point, it took about 60 s for the voltage to become stable. All the performance tests were performed at room temperatures of 23.0–24.0 °C and relative humidity of 63–70%. Prior to the experiment, each MEA was activated for 12 h at 60 °C.

To measure the water recovery flux, the cathode fixture was changed to an active mode and a water trap filled with Drierite (anhydrous CaSO$_4$) was connected. The water was gathered at a constant current density for 8.0 h. The details about this test could be found from [17].

4. Results and discussion

Sufficient water produced at the cathode must be passively transported to the anode to supply the required water for the anodic MOR. The corresponding water flux depends on the capillary pressure created by the cathode MPL as discussed in Section 2. However, conventional MPLs made of carbon powder suffer from the problem of mud-cracks [18–20]. These macro cracks significantly increase the permeability ($K$) of the cathode MPL, reducing the capillary pressure. To tackle this issue, nanotube materials were adopted, since the two-dimensional structure of nanotubes has better interaction to form the MPLs. Furthermore, it is understood that the low surface energy of the material is the key to
superhydrophobicity (contact angle >150°) and fluorine is effective for lowering the surface free energy [21–23]. Therefore, to increase the hydrophobicity, the carbon nanotubes were fluorinated through chemical modification as shown in Fig. 1 to achieve a super-hydrophobic MPL.

The surface morphologies of the MPLs made of different carbon materials (denoted by carbon powder MPL, nanotube MPL, fluorinated nanotube MPL) are shown in Fig. 3. From these SEM images, it can be seen that the MPLs made of MWCNTs and fluorinated MWCNTs are free of mud-cracks. As compared, a large number of mud-cracks with a width of around 10–20 μm are formed on the whole surface of the carbon powder MPL.

The EDX spectrum of the fluorinated nanotube MPL is shown in Fig. 4. In the EDX spectrum, all the elements from the functional group, F, O and Si, were detected, indicating the hydrophobic functional groups (F_12C_10H_9Si–) were successfully introduced onto the carbon nanotubes as shown in Fig. 1.

Fig. 5 shows the contact angles of various MPLs. It can be seen that the hydrophilic or hydrophobic functional groups on the surface of carbon nanotubes significantly influence the wettability of the MPL. The contact angle of the carbon powder MPL is 142.4°, much smaller than that of the MPL adopting fluorinated MWCNTs. The contact angle of the fluorinated nanotube MPL is as high as 153.2°, suggesting that a super-hydrophobic cathode MPL was achieved.

Fig. 6 compares the cell performance of the DMFCs with various cathode MPLs under the neat methanol operation. As indicated in Fig. 6, the macro cracks and the hydrophobicity of the cathode MPL significantly influence the cell performance. The DMFC adopting the hydroxylic nanotube MPL with the lowest hydrophobicity shows the worst performance, but the DMFC with the crack-free nanotube MPL yields better performance than the carbon powder one. More importantly, the DMFC with the fluorinated nanotube MPL with a crack-free and super-hydrophobic surface shows the best performance. The peak power density reaches 25.6 mW cm⁻², improving more than 30% compared with the carbon powder one which is 19.4 mW cm⁻². For the DMFCs with various MPLs, the internal resistances are 51.9 mΩ (fluorinated nanotube), 53.8 mΩ (nanotube), 55.1 mΩ (carbon powder) and 59.2 mΩ (hydroxylic nanotube). The fact indicates that there is no obvious difference among the internal resistances. Hence, the significant improvement can be attributed to the fact that the fluorinated nanotube MPL can help to build a larger capillary pressure than the conventional one, enhancing the water back transport. The increased water back flux improves the kinetics of the anodic MOR, thereby boosting the cell performance. To further investigate the performance improvement, the anode and the cathode overpotentials are compared in Fig. 7. It shows that the performance difference mainly occurs at the anode rather than at the cathode. The difference among the anode overpotentials increases.

![Fig. 7. Overpotential curves of the DMFCs with various MPLs: (a) anode overpotential and (b) cathode overpotential.](image)

![Fig. 8. Water transport flux from the cathode to the anode with various MPLs.](image)

![Fig. 9. Transient discharging behaviors of the DMFCs at the current density of 80 mA cm⁻² with various MPLs.](image)
with increasing the current density. In addition, it can be observed that the mass transfer limit occurs at the anode only and the limiting current density increases from 120 mA cm\(^{-2}\) to 145 mA cm\(^{-2}\), indicating the mass transfer limit of the DMFCs under the neat methanol operation is due to the lack of water for MOR, as the methanol supply rate were kept the same during all the tests. This finding is consistent with that in a previous study [24]. The above-mentioned results suggest that the fluorinated nanotube MPL can improve anodic MOR by enhancing the water back transport compared with the conventional MPL structure.  

To further confirm the effect of fluorinated nanotube MPL on water transport, the water recovery fluxes with different MPLs are compared in Fig. 8. It indicates that there is a significant increase in the water back flux after replacing the conventional carbon powder MPL with the fluorinated nanotube MPL. For instance, at the current density of 40 mA cm\(^{-2}\), the water recovery flux of the DMFC with the fluorinated nanotube MPL is 0.326 \(\mu\)mol s\(^{-1}\) cm\(^{-2}\), 27\% larger than the carbon powder one with a flux of 0.256 \(\mu\)mol s\(^{-1}\) cm\(^{-2}\). At a constant current density of 80 mA cm\(^{-2}\), the transient discharging behaviors of the DMFCs with different cathode MPLs are shown in Fig. 9. It shows that all the voltages are rather stable and more importantly, the cell voltage improves significantly with the adoption of the fluorinated nanotube MPL. The fact suggests that the crack-free and super-hydrophobic MPL is effective for improving the water management of passive DMFCs operating with neat methanol.

5. Conclusions

Water management is particularly important for the passive DMFCs operating with neat methanol, as the water generated at the cathode must be passively transported to the anode at a sufficiently large flux to compensate the required water for the MOR. In this work, we fabricated the cathode MPL with fluorinated carbon nanotubes and demonstrated that the MPL is crack-free and super-hydrophobic. It is shown that the application of the modified MPL to a passive DMFC operating with neat methanol enables a significant increase in the water recovery flux, improving the anodic methanol oxidation reaction and thereby boosting the cell performance.

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