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Effects of structural aspects on the performance of a passive air-breathing direct methanol fuel cell

Yong Tang, Wei Yuan*, Minqiang Pan, Biao Tang, Zongtao Li, Zhenping Wan

School of Mechanical and Automotive Engineering, South China University of Technology, Wushan Road 381, Guangzhou 510640, Guangdong, People's Republic of China

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ABSTRACT

This study systematically investigates the effects of structural aspects on the performance of a passive air-breathing direct methanol fuel cell (DMFC). Three factors are selected in this study: (1) two different open ratios of the current collector; (2) two different assembly methods of the diffusion layer; and (3) three membrane types with different thicknesses. The interrelations and interactions among these factors have been taken into account. The results demonstrate that these structural factors combine to significantly affect the cell performance of DMFCs. The higher open ratio not only provides a larger area for mass transfer passage and facilitates removal of the products, but also promotes higher methanol crossover. The hot-pressed diffusion layer (DL) can mitigate methanol permeation while the non-bonded variant is able to enhance product removal. The increase of membrane thickness helps obtain a lower methanol crossover rate and higher methanol utilisation efficiency, but also depresses cell performance under certain conditions. In this research, the maximum power density of 10.7 mW cm^{-2} is obtained by selecting the current collector with a lower open ratio, the non-bonded DL, and the Nafion 117 membrane. The effect of methanol concentration on the performance of DMFCs is also explored.

1. Introduction

In recent years, the direct methanol fuel cell (DMFC) based on a passive fuel feeding anode and an air-breathing cathode has attracted increasing attention in the fuel cell community. It is regarded as a promising candidate that could replace the conventional battery for portable electronic applications [1–3] due to its high energy density, compact configuration, low emission and easy refueling. In general, a passive air-breathing DMFC consists of an anode immersed in a liquid fuel reservoir and a cathode exposed directly to the ambient atmosphere. This special architecture makes it possible for the DMFC to generate power without external balance-of-plant (BOP) devices such as liquid pumps, air blowers, heat exchangers and so on, thereby eliminating parasitic power losses, resulting in a higher volumetric power density and overall efficiency of the fuel cell system.

With the development of passive DMFCs, common issues (e.g. water and methanol crossover, lower electro-catalytic activity and higher noble metal loading) also dominate the behaviour of this fuel cell. In the past decade, considerable efforts were made to deal with difficulties related to water, heat and gas management, and methanol transport. As opposed to the direct hydrogen fuel cell, the DMFC faces the additional problem of methanol crossover. In DMFCs, methanol tends to permeate through the electrolyte membrane and be oxidised on the cathode side, leading to a mixed potential [4] which ultimately reduces the fuel cell performance. Moreover, methanol crossover causes substantial fuel waste and energy losses, inhibiting the reactant utilisation and system efficiency. Another challenge is the transport and removal of water. In DMFCs, the aqueous methanol solution forms an environment full of liquid water, resulting in acute water crossover through the membrane. Thus water may increasingly build up in the diffusion layers and flow channels, impeding the reactant transport to the catalyst layers. This restrains the reactions and finally degrades the cell performance. In addition, the vent of carbon dioxide produced at the anode is also an issue that needs to be well managed to prevent bubble block along the methanol feed path. These issues are greatly affected by structural aspects of the membranes, diffusion layers (DLs), and current collectors.

Some previous work demonstrated that membrane thickness was a key factor that significantly affected the methanol and water crossover, as well as water back-diffusion [5–9]. It is well known that the membrane thickness both affects the methanol permeation rate and the water transport coefficient. Generally, a thicker membrane is preferred because it decreases methanol permeability. However, a thicker membrane also brings a higher mass transfer resistance. This may reduce the cell performance to some extent. On the other hand, a thinner membrane may improve the cell performance, because the effect of the increased methanol permeability could be compensated by the dilution effect of the water back flow.

* Corresponding author. Tel.: +86 2085516947; fax: +86 2085516947.
E-mail address: yuanweijob@yahoo.com.cn (W. Yuan).

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To sum up, there should be an optimum value of the membrane thickness to maintain the mass transfer balance in the DMFC with various assembly configurations. Therefore, a reasonable selection of membrane type depends on a comprehensive evaluation of the effects of the fuel cell structure. In other words, the interactive relationship between the membrane and other components should be taken into account for fuel cell design and optimisation.

In a passive air-breathing DMFC, the concept of traditional flow field evolves into a somewhat open pattern, as presented by many other research groups [2,6,10], because the machined blind-channels on the bipolar plates are not suitable for the reactant delivery. A popular way to address this problem is to fabricate perforated holes or through-channels on the metal plates, which act as both current collectors and reactant distributors. In this case, the free open ratio of the current collector is an important factor influencing the mass transfer characteristics of DMFCs, especially for a passive system. However, information in the literature relating to this issue is still limited. Chang and co-workers [11,12] designed current collectors with a series of fractal geometry. They pointed out that the higher open area ratio and longer total hole perimeter length on the bipolar plate could facilitate increased cell performance. Although their DMFC was actively operated, the results were still of great significance to passive DMFC design.

Another necessary part of a DMFC is the diffusion layer which is used to distribute the reactants from the flow field to the catalyst layer (CL). It forms a porous medium zone between the reaction area and flow field. This zone plays an important role in the mass transfer process. In a typical DMFC with passive operation, the DL is usually exposed directly to the fuel chamber at the anode and the ambient environment at the cathode. This special configuration of a passive DMFC makes its diffusion properties quite different from an active DMFC. The DL in a passive DMFC should be more helpful in providing fluxes of the reactants appropriately and remove the reaction products efficiently. Extensive work has been done to optimise the interior structures and composition, using materials such as carbon and PTFE loadings. These optimisations are especially important for the micro-porous layer (MPL) integrated in the DL [7,13–15]. However, very little research has been dedicated to the assembly method of the DL, particularly when a catalyst-coated membrane (CCM) is used. The application of a CCM enables the DL to be installed either in hot-pressed or non-bonded form because the catalyst is not spread on the DL. With regard to engineering practices, the effects of these two assembly methods appear to be both attractive and significant, so this process deserves systematical comparative study. From the above review, it can be seen that the membrane, current collector and DL all have great influence on the cell performance for a DMFC. However, previous research focused only on individual effects of these key components with isolated analyses.

In this study, the effects of the membrane, diffusion layer and current collector, as well as their interactions are comprehensively investigated through a series of comparative experiments. They are treated as three barriers affecting the mass transfer activities. Three parameters are studied: the open ratio of the current collector, the assembly method of the diffusion layer, and membrane thickness. The influence of methanol concentration on cell performance is also discussed.

2. Experimental

2.1. Fabrication of the membrane electrode assembly (MEA)

In this study, three types of Nafion® perfluorosulfonic acid (PFSA) membranes, NR212, N115, and N117 (DuPont, Inc.), were employed as the solid electrolyte. The backing layer (BL) was composed of TGP-H-060 carbon paper (Toray, Inc.). The MEAs with an active area of 9 cm^2 (3 cm × 3 cm) were fabricated by CCM method. The catalyst loadings were 4 mg cm^{-2} Pt–Ru with 1:1 nominal atomic ratio on the anode side and 2 mg cm^{-2} Pt on the cathode side, respectively. The detailed fabrication process is described here. First, the membrane was boiled in 3 wt.% H_2O_2 aqueous solution for 1 h and then in deionised (DI) water for 1 h, followed successively by 0.5 M H_2SO_4 aqueous solution to activate the membrane. The membrane was then purified by boiling again in DI water to remove any residual sulfuric acid. For DL preparation, a layer containing a mixture of PTFE/C (Vulcan XC72, E-TEK, Inc.) was bonded to the surface of the wet-proofed BL to form a complete DL. The catalyst ink for the electrodes was prepared by mixing the catalyst powders (Johnson Matthey, Inc.), Nafion® solution, and isopropyl alcohol together. Subsequently, the catalyst layers were uniformly coated on both sides of the pre-treated membrane by using spraying machine. Two types of MEAs were made and tested in the present work, as shown in Fig. 1. The first type was a CCM with two DLs hot-pressed together at 120 °C and 10 MPa for 2 min. The second type was a single CCM sandwiched between two DLs with non-bonded assembly method for the DMFC.

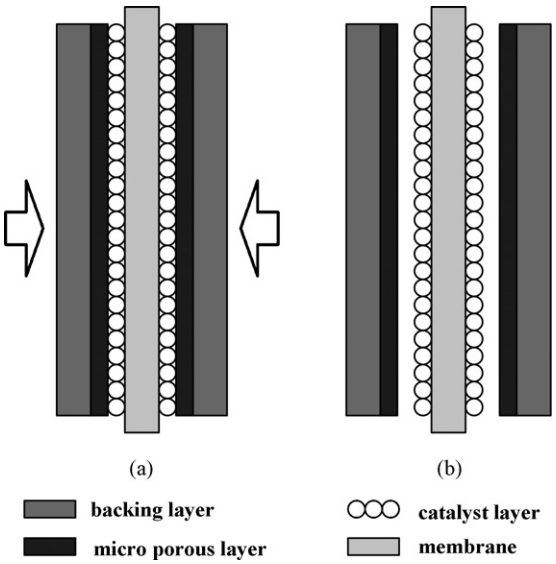

Fig. 1. A schematic diagram of the MEAs with two different assembly methods of the diffusion layers: (a) hot-pressed DL (HPDL); (b) non-bonded DL (NBDL).

2.2. Configuration of the single direct methanol fuel cell (DMFC)

The single DMFC was made up of an anode fuel chamber, a cathode end frame, current collectors, GDLs, a MEA and gaskets. Fig. 2 shows an exploded view of the configuration of the single DMFC. In this work, transparent polymethyl methacrylate (PMMA) material was used to make the end plates on both sides by using milling and polishing techniques. This allowed the visualization of the internal activity and also provided sufficient rigidity to support the unit cell. A built-in reservoir with a volume of 10.8 mL was machined on one side of the anode end plate for methanol solution storage. Two small holes were drilled on the upper side for fuel injection and gas exhaust. The cathode end plate was shaped like a hollow frame, allowing the ambient air to diffuse to the electrode surface through spontaneous convection.

The current collector was made of stainless steel (SS) 316L, which has proven to have acceptable performance in both electrical conductivity and corrosion resistance [2,11,12,16]. As mentioned above, in a passive DMFC system, grooved flow channels are always replaced by an array of holes in the current collector. In this study, a

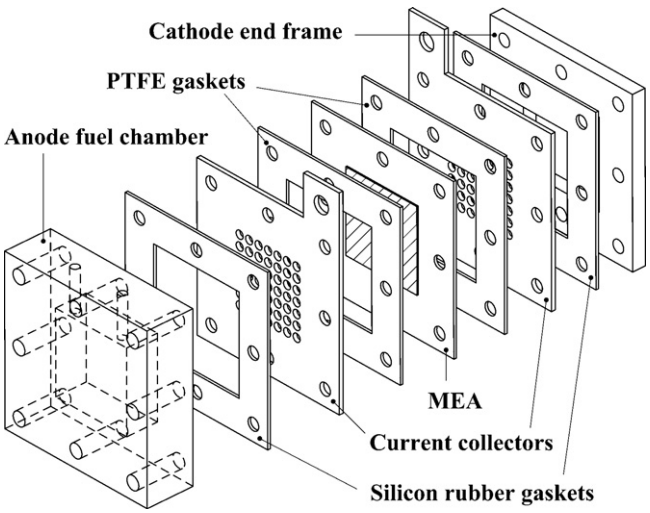

Fig. 2. A schematic diagram of the configuration of the passive air-breathing DMFC.

Table 1
Geometric characteristics of the two different circular-hole arrays.

Current collector type	CHA-1	CHA-2
Hole diameter/mm	3	1.5
Hole number	49	144
Free open ratio/%	38.5	28.3

circular-hole array (CHA) pattern was adopted to provide access for the fuel and oxidant. The CHA dimension was kept within the range of the reaction area. Here, two types of current collectors were fabricated by changing the hole size and hole number to obtain two different open ratios, as shown in Table 1 and Fig. 3.

The gasket is necessary to prevent leakage of the reactant solution between the fuel cell components such as the MEAs, current collectors and end plates. Material selection and thickness design of the gasket are two critical factors that have to be considered carefully to ensure sealing quality and reduce contact resistance [2]. In this work, silicon rubber with a thickness of 0.5 mm was placed between the current collector and the end plate, while an in-house PTFE thin film was used as the gasket to seal between the current collector and the edged membrane of the MEA. The thickness of the PTFE gasket can be modified conveniently through a standardised fabrication process according to the requirements for different MEA configurations. The gaskets were tested under a proper compressive stress applied by using eight M4 screw bolts, and were proven to work well.

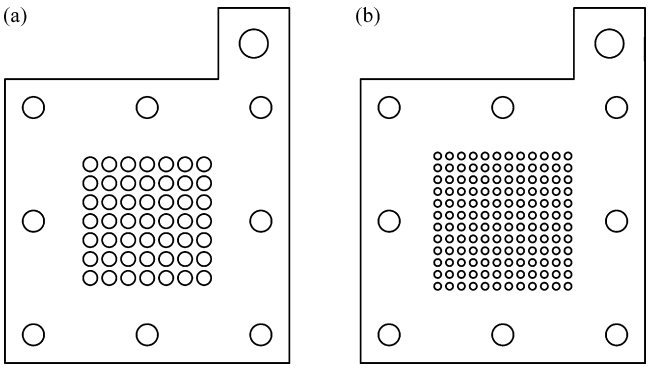

Fig. 3. A schematic diagram of the current collectors with two different open ratios: (a) CHA-1; (b) CHA-2.

Table 2
Basic parameters of the different types of Nafion membranes [17].

Membrane type	Typical thickness/μm	Basis weight/gm^{-2}
Nafion 212	50.8	100
Nafion 115	127	250
Nafion 117	183	360

2.3. Experimental setup and strategy

An electronic load was employed to provide a discharging function and measure the current and voltage variations. The results of the cell performance were recorded by data acquisition (DAQ) software and characterised using polarisation curves, plotting current vs. voltage (*I–V*) and current vs. power (*I–P*). The galvanodynamic method was used with a constant scan rate of 1 mA s^{-1}. Methanol was fed into the fuel reservoir at the anode compartment using liquid injectors with standard volume scales. No peripheral equipment was needed. Before each test, the fuel reservoir was cleaned with DI water and dried at normal temperatures to eliminate the influence of previous experiments. Each MEA underwent an activation process under a constant load for 12 h. All the experiments were carried out at a room temperature of around 28 °C and a relative humidity of approximately 85%.

The current collector, DL and membrane are three structural barriers that the methanol and water have to pass through when they migrate between both sides of the membrane. To explore the effects of these structural aspects and their related interactions in the DMFC, the following configurations were designed: three types of membranes with different thicknesses (see Table 2); two assembly methods of the DLs, including the hot-pressed DL (HPDL) and the non-bonded DL (NBDL); and two samples of current collectors with different open ratios (see Table 1 and Fig. 3). Here, it was assumed that the anode and cathode had the same setup of DLs and current collectors. Thus, there were twelve configuration cases in total, produced by various arrangements of the experimental variables. For each configuration, the methanol concentration was tested at 0.5, 2, 4, and 8 M. In addition, the surface morphologies of both the hot-pressed and non-bonded DLs were characterised using scanning electron microscopy (SEM).

3. Results and discussion

When discussing the effects of the structural conditions on the cell performance, the polarisation (*I–V*) and power density (*I–P*) curves are typically selected from the experimental data obtained at 2 M methanol concentration. Fig. 4 lists the open circuit volt-

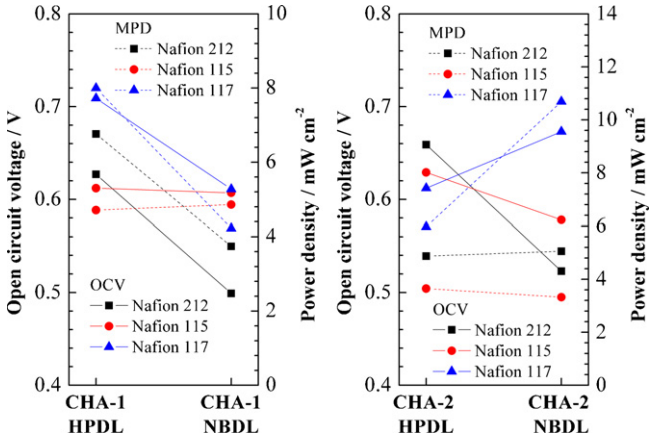

Fig. 4. Open circuit voltages and maximum power densities of the DMFC with various structural parameters.

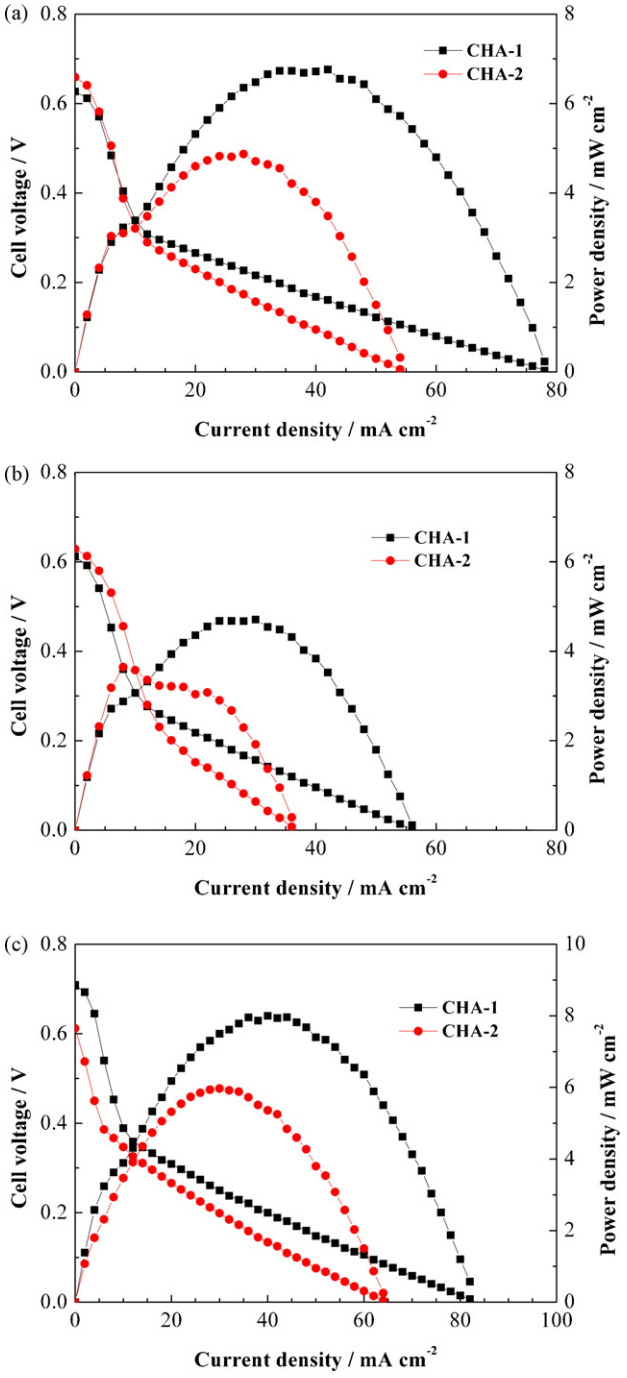

Fig. 5. Performance comparison of the passive DMFC with two different open ratios of the current collector when HPDL is used: (a) Nafion 212; (b) Nafion 115; (c) Nafion 117.

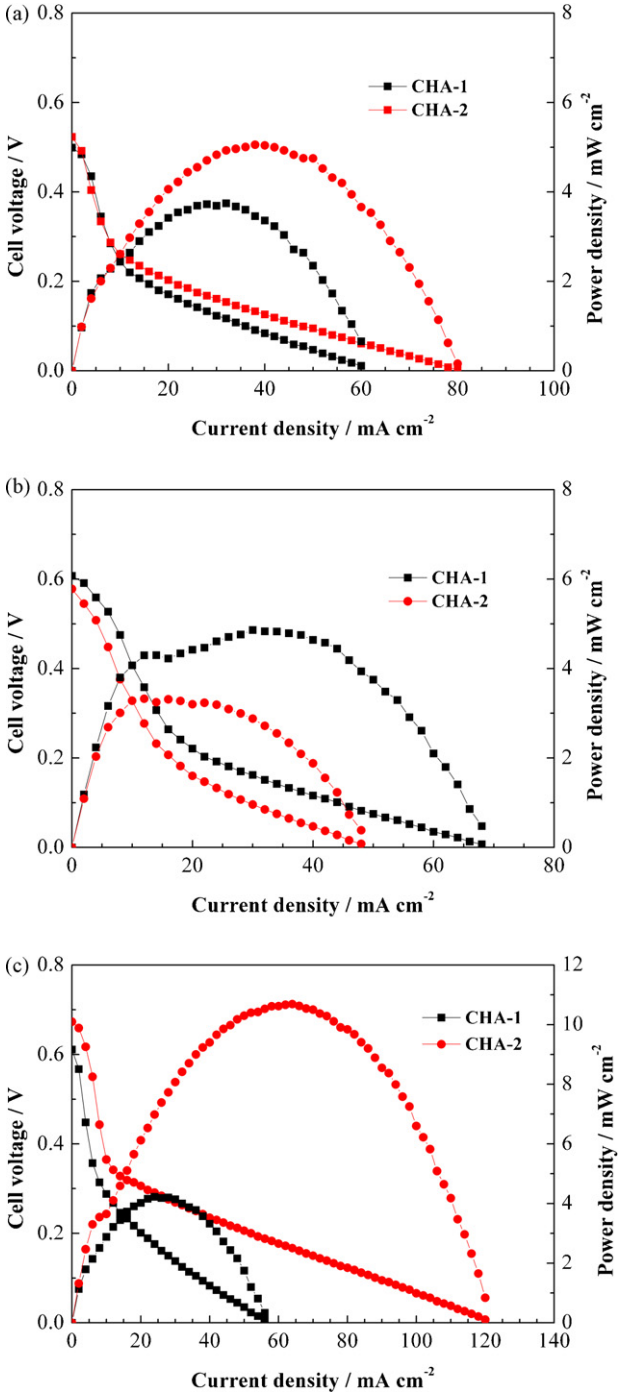

Fig. 6. Performance comparison of the passive DMFC with two different open ratios of the current collector when NBDL is used: (a) Nafion 212; (b) Nafion 115; (c) Nafion 117.

ages (OCVs) and the maximum power densities (MPDs) for various cases when 2 M methanol solution is supplied. These resulting parameters highlight the changes caused by different structural combinations.

3.1. *Effect of the open ratio of the current collector*

Figs. 5 and 6 illustrate the *I–V* and *I–P* curves of the passive DMFC with different open ratios of the current collector. For CHA-1 shown in Fig. 5, the maximum power densities of the passive DMFCs with Nafion 212, 115, and 117 are 6.8, 4.7 and 8.0 mW cm^{-2}, respectively. Correspondingly, for CHA-2, the maximum power densities of the passive DMFCs are only 4.9, 3.6 and 6.0 mW cm^{-2}, respectively. It is obvious that a higher open ratio of the current collector helps enhance the cell performance, especially when HPDL is utilised. It is observed that the cell voltage for CHA-1 decreases more slowly with the increase of current density than CHA-2. This phenomenon can be attributed to the mass transfer improvement caused by larger area of the holes. On one hand, a higher open ratio facilitates methanol, water and oxygen diffusion from outside to the electrode surface area. On the other hand, it also provides an efficient vent path for the produced gas bubbles and excessive water. Contrarily, the current collector with a lower open ratio may lead to reactant

starvation in the catalytic reaction area at both sides, gas block at the feed path of the anode, as well as water flooding at the cathode. Moreover, it is also found by observing the results in Fig. 5 that the difference of the OCV between CHA-1 and CHA-2 is not prominent, which implies that the methanol crossover is still under control to a reasonable degree, regardless of the open ratio change. Under this condition, a higher open ratio of the current collector is preferable for better mass transfer characteristics. Compared with the active DMFC [11,12], the passive fuel cell in this work seems more sensitive to the open ratio of the current collector because of the passive air-breathing operation mode.

However, it can be seen in Fig. 6 that the results appear to be contrary to the results shown in Fig. 5 when HPDL is replaced with NBDL. For CHA-1, the maximum power densities of the passive DMFCs with Nafion 212, 115, and 117 are 3.7, 4.9 and 4.2 mW cm^{-2}, respectively. Comparatively, for CHA-2, the maximum power densities of the passive DMFCs are 5.0, 3.3 and 10.7 mW cm^{-2}, respectively (see Fig. 6). These distinct changes demonstrate that a lower open ratio also has the ability to increase the cell performance under certain conditions. This interesting result can be explained by the following reasons. First, a lower open ratio leads to reduced permeability of the reactant distributor which benefits the reactant utilisation especially on the anode side. Secondly, the DL assembly method (see Section 3.2) seems to be the most dominant factor influencing the cell performance trend. Compared with Fig. 5, a drop in the OCV is observed in Fig. 6, which suggests that the methanol crossover becomes more severe than with the HPDL construction. Under this condition, a higher open ratio apparently increases the methanol crossover and thereby reduces the cell performance, but a lower open ratio is able to offset this effect or even enhance the cell performance efficiently. This mechanism can explain why the cell performance drops sharply for CHA-1 and grows rapidly for CHA-2. Meanwhile, it is noticed that the performance changes are less remarkable for the DMFC with the Nafion 115 membrane, because the internal mass transfer balance is still maintained at a relatively stable level through mutual restrictions among the involved factors. Therefore, it can be concluded that, as the first structural barrier, the open ratio of the current collector has dual effects on the performance of the passive DMFC. It can also be inferred that the cell performance of the passive air-breathing DMFC depends on a collective function of the three components: current collector, DL (see Section 3.2) and membrane (see Section 3.3), rather than any individual aspect. Detailed analyses on the effects of the DL and membrane are given in the following sections.

3.2. Effect of the assembly method of the diffusion layer

As the second structural barrier, the DL also exerts significant influence on the cell performance in the DMFC. When the CCM type is used, the assembly method of the DL is particularly important to the cell performance. Figs. 7 and 8 present the polarisation and power density curves of the passive DMFC with two different DL construction methods. Fig. 7 shows that the cell performance of the DMFC with HPDL exceeds that with NBDL when CHA-1 is utilised, though the Nafion 115 membrane still maintains a similar performance under both conditions. With the increase of the open ratio of the current collector, the permeation of the methanol solution increases accordingly, intensifying the burden on the second barrier, the DL. In this case, the HPDL is more able to prevent excessive methanol crossover because of its dense structure when combined closely with the catalyst layer of the MEA. Fig. 9 shows the SEM results comparing the surface morphologies of both the hot-pressed and non-bonded DLs. It can be seen that the hot-pressing process makes a substantial amount of carbon fibers in

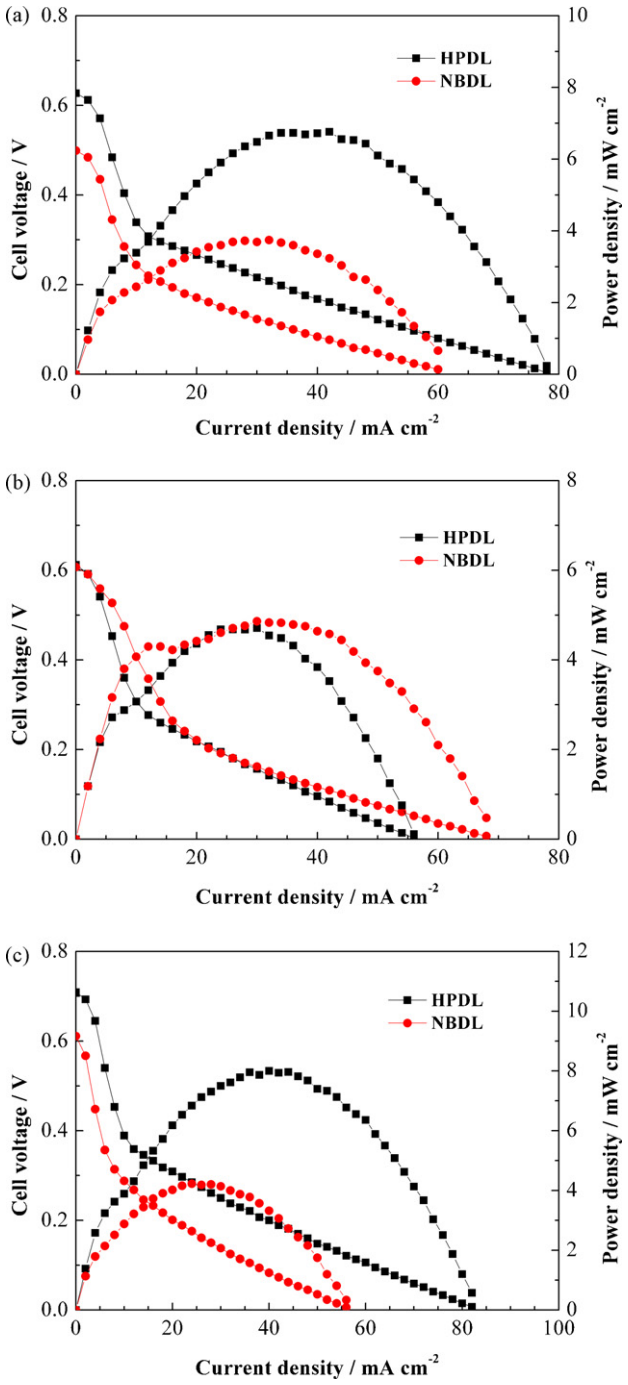

Fig. 7. Performance comparison of the passive DMFC with two different assembly methods of the diffusion layer when CHA-1 is used: (a) Nafion 212; (b) Nafion 115; (c) Nafion 117.

the BL and agglomerate mixtures in the MPL crushed into small pieces. These structures could plug up the macro/micro pores of the porous network. Moreover, the compression force clumps the substrate and MPL together so that the electrodes become more compact and impermeable [18]. This leads to a reduced porosity of the MEA with HPDL. Apparently, such a compact structure helps restrict mass transport [18,19], thereby mitigating the methanol permeation through the diffusion layers. Conversely, the porous structure of the non-bonded DL remains unbroken with a higher porosity, which makes the methanol crossover appear more severe so that the cell performance is reduced to a lower level, as mentioned in Section 3.1. Thus, the HPDL contributes to performance

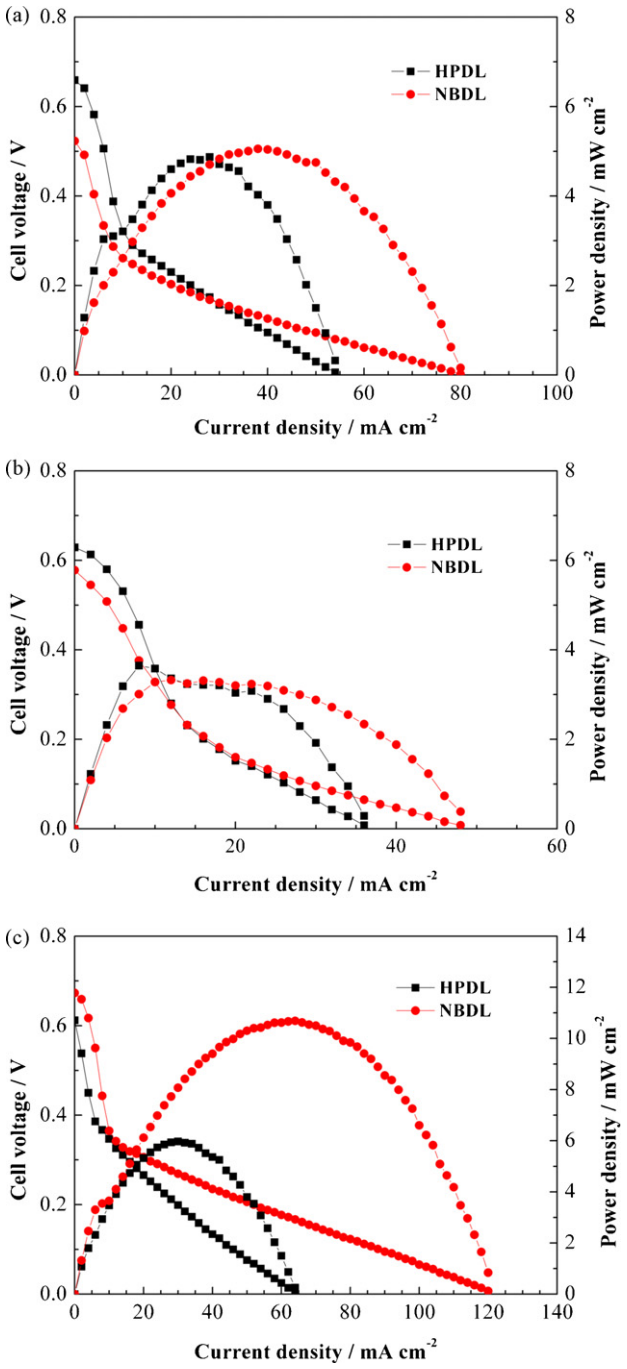

Fig. 8. Performance comparison of the passive DMFC with two different assembly methods of the diffusion layer when CHA-2 is used: (a) Nafion 212; (b) Nafion 115; (c) Nafion 117.

enhancement of the passive DMFC when the methanol permeation turns into a critical issue.

On the other hand, it is seen from Fig. 8 that, when CHA-2 is used, the cell performance of the DMFC with NBDL recovers and consequently yields a better performance than with HPDL. The power output of the latter loses 1.6 mW cm^{-2} on average, in contrast to the results in Fig. 7. This performance alteration can be interpreted as a change in the internal mass transfer condition in the passive DMFC. When a lower open ratio is adopted, the product removal becomes the dominant issue, rather than the methanol crossover. At the anode, CO_2 bubbles are generated through the methanol oxidation reaction (MOR), while at the cathode, water is also produced through the oxygen reduction reaction (ORR). If these products cannot move out due to the small permeability of the current collector and DL, they will accumulate and block the feed paths. This means that reactions at both sides cannot work well due to a lack of sufficient reactants, especially for such a passive air-breathing DMFC. Thus, under this condition, the NBDL is the optimal choice because of its mass transfer improvement. The NBDL has a more open structure that can provide a buffer area, facilitating the penetration of the CO_2 bubbles and residual water. Therefore, when current collector itself cannot lead the product removal successfully (e.g. CHA-2), a DL with the non-bonded assembly method provides a tuned layer to regulate the mass transfer characteristics. These results indicate that the current collector and the DL complement each other. This rationale agrees well with that proposed in Section 3.1. Besides, the pronounced performance recovery is also beneficial because the catalyst layer is protected from being destroyed by the hot-pressing force. The original catalyst morphology can be retained so as to elevate the reaction efficiency in the zone of the three-phase interface when the electrode suffers a higher mass transfer resistance. So it is understandable that some groups use only carbon paper without a MPL to reduce mass transfer resistance [20]. In the present work, we observe acceptable results with both the combination of CHA-1 and HPDL, and CHA-2 and NBDL, when Nafion 117 is employed. The latter provides a better maximum power density of 10.7 mW cm^{-2}. In addition, the Nafion 115 membrane is tolerant to the different DL assembly methods, although its performance is not quite acceptable. This result suggests that the membrane type is also a contributing factor that needs to be considered.

3.3. *Effect of the membrane thickness*

It is well known that membrane thickness has a significant effect on the cell performance of the DMFC both in both passive and active systems. In this paper, the membrane is treated as the third barrier in mass transfer paths. However, when the effects of other components such as the current collector and the DL on mass transfer are considered simultaneously, the dominating mechanisms may be different. Figs. 10 and 11 present the performance curves of the passive DMFC with the various membranes. Two different current collector open ratios and two different DL assembly methods are used to explore the interactions among the three factors. It is shown in Fig. 10(a) that when CHA-1 and HPDL are used, the cell performances are in the order Nafion 117 > Nafion 212 > Nafion 115. Usually, the thicker membrane is beneficial to performance improvement as a result of a slower methanol crossover rate. Also, the methanol utilisation efficiency is known to increase with an increase in membrane thickness [6,8]. Thus, Nafion 117 yields the best cell performance, as expected. However, the performance of Nafion 115 is actually worse than that of Nafion 212, which deviates from the normal result as reported in active systems [5]. The reason for this phenomenon can be explained when considering the precondition that in addition to the membrane, other components also exert an influence on cell performance, especially when the DMFC is passively operated. The DMFC with combined CHA-1 and HPDL is able to handle the methanol permeation at a reasonable level before the methanol permeates through the membrane, so that the methanol crossover rate is not excessively high. Under this condition, the thinner membrane can further reduce the methanol crossover through back-diffusion of water, which can mitigate the cell performance degradation. In this regard, the intermediate thickness of Nafion 115 suffers performance degradation from both a reduction in water back-diffusion compared to the thinner membrane Nafion 212, and a worse methanol transfer resistance compared to the thicker membrane Nafion 117. In other words, Nafion 115 is somewhat insensitive to the degree of

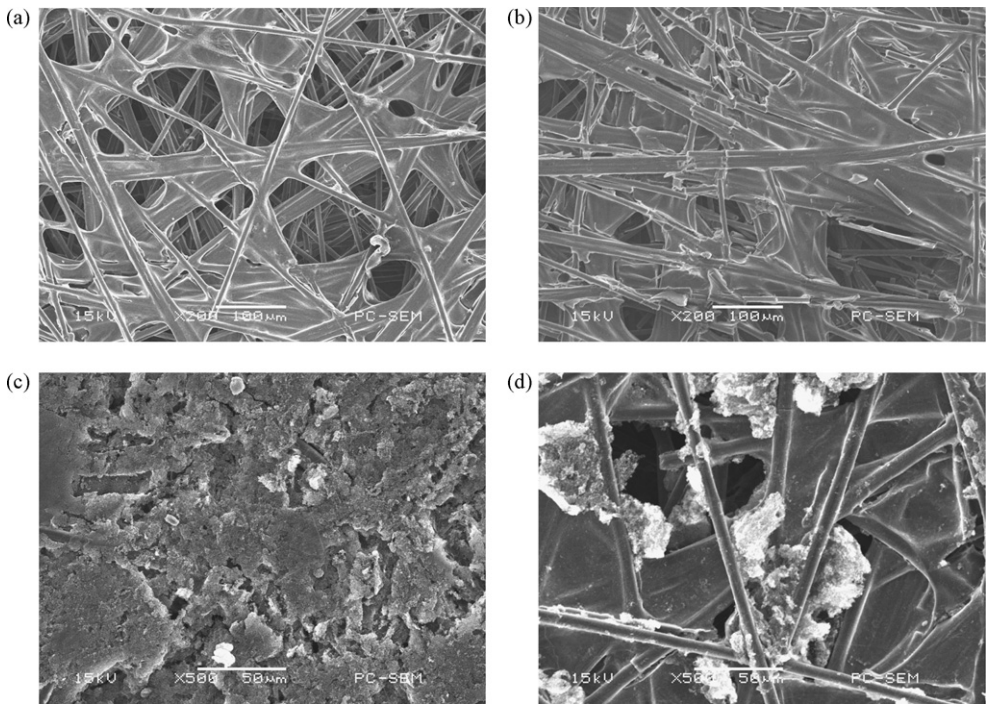

Fig. 9. SEM images of the surface morphologies of NBDL and HPDL: (a) BL in NBDL; (b) BL pieces in HPDL; (c) MPL in NBDL; (d) MPL pieces in HPDL.

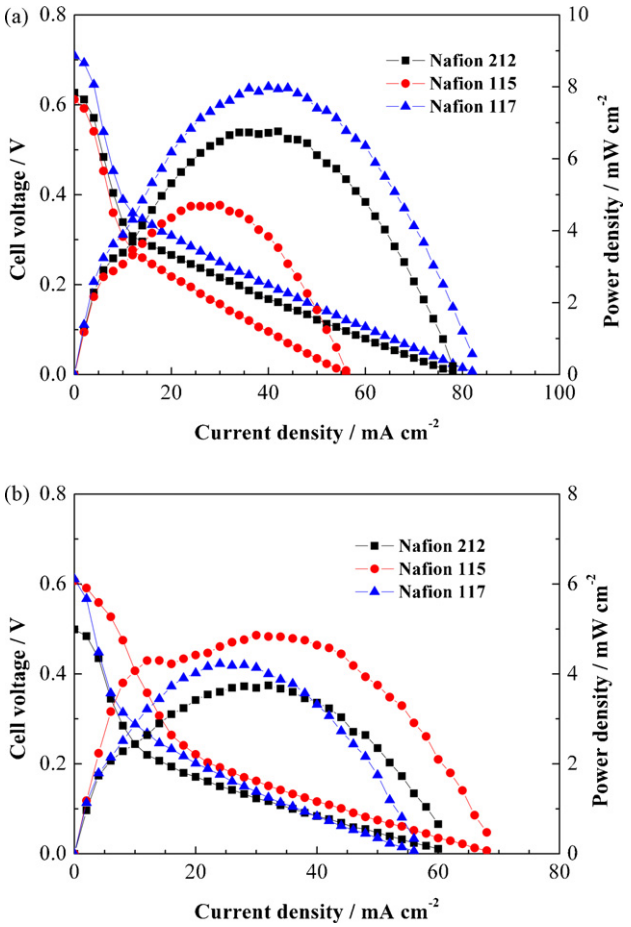

Fig. 10. Performance comparison of the passive DMFC with three different types of the Nafion membranes: (a) CHA-1 and HPDL; (b) CHA-1 and NBDL.

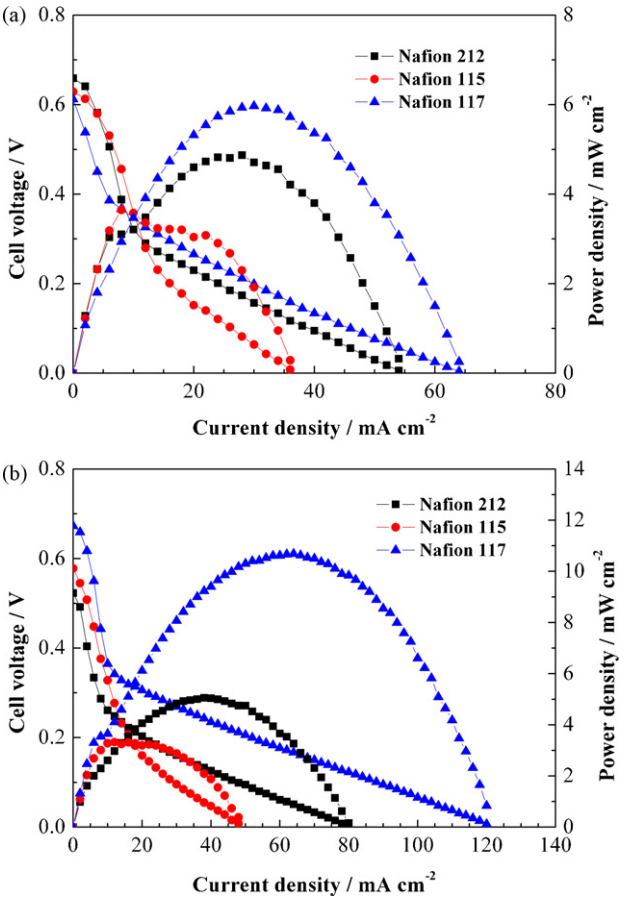

Fig. 11. Performance comparison of the passive DMFC with three different types of the Nafion membranes: (a) CHA-2 and HPDL; (b) CHA-2 and NBDL.

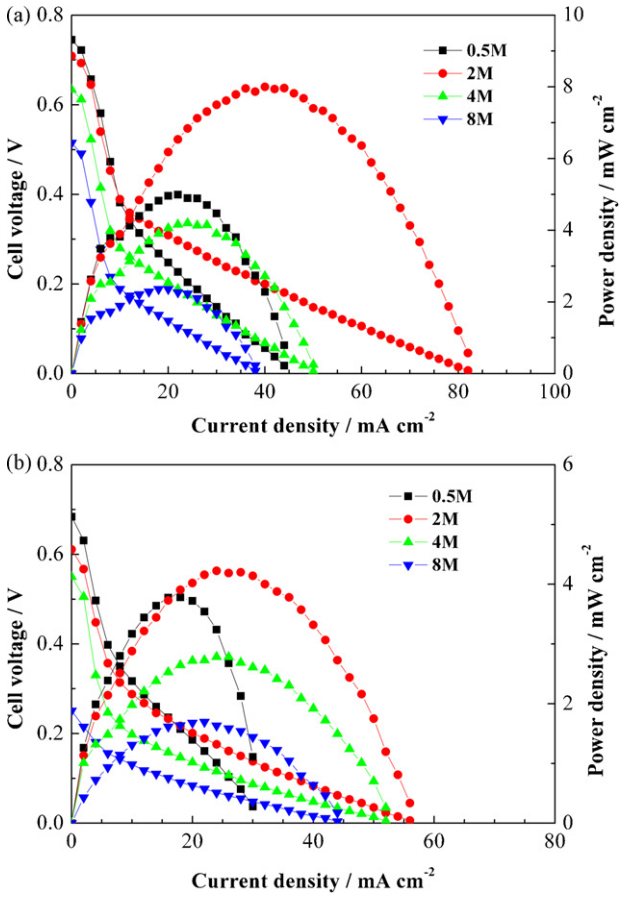

Fig. 12. Performance comparison of the passive DMFC with Nafion 117 membrane at different methanol concentrations: (a) CHA-1 and HPDL; (b) CHA-1 and NBDL.

the methanol crossover driven by a change in real structural conditions. However, when methanol crossover occurs excessively, the insensitivity of Nafion 115 may become an advantage for the maintenance of the cell performance. For example, it is noted in Fig. 10(b) that when CHA-1 and NBDL are used together, Nafion 212 and 117 both suffer an extreme performance decrease as a result of the acceleration of the methanol crossover rate, but correspondingly Nafion 115 still works in a relatively steady state as before. It is shown that the performance of Nafion 117 is even lower than Nafion 115, which proves again that a high mass transfer resistance can also be a defect that reduces cell performance [8]. Therefore, it can be inferred that the advantages and disadvantages of the mass transfer characteristics of the membrane are organically connected and depend strongly on the presence of other components.

It is obvious in Fig. 11 that Nafion 117 exhibits the highest performance among the three membranes when CHA-2 is utilised. Under this condition, methanol crossover is not a dominant issue because methanol permeation is hindered by a lower open ratio of the current collector. But when the HPDL is used, the effect of the hot-pressed DL is regarded as the main factor controlling the methanol permeation as well as limiting the removal of gas bubbles and produced water due to such a compact configuration. Thus, the cell performance curves of the DMFC with various membranes behave in a manner depicted in Fig. 10(a), which also uses the HPDL. When the NBDL is used (see Fig. 11(b)), the gas and water removal are improved, especially at high current densities, but the methanol permeation rate increases due to the use of the non-bonded DL assembly method. Hence the ultimate cell performance depends on which factor is more effective. Under this condition, the performance of the DMFC with Nafion 117 increases rapidly to the maximum output value among all the MEAs tested. This performance change derives from an improvement in the internal mass transfer characteristics. On the other hand, compared with Fig. 11(a), although Nafion 212 and 115 both achieve higher performances at high current densities, the differences in the maximum power output are still very marginal. Therefore, it can be concluded that the effect of the membrane thickness mainly lies in the alteration of the amount of methanol and water crossover fluxes. When other structural parameters are changed, the membrane reacts in a modified manner and then a new mass transfer balance is realised through complex interactions among the other structural factors. The final performance is determined by the dominant factor which controls the mass transfer processes in each stage. To sum up, Nafion 117 is recommended to achieve a high performance in a passive air-breathing DMFC.

3.4. Effect of the methanol concentration

The data obtained from the passive DMFC with Nafion 117 are selected to affirm the effect of the methanol concentration, as described in Figs. 12 and 13. It is obvious from these figures that the OCV decreases regularly with an increase in methanol concentration. In all structural configurations, the 0.5 M methanol solution yields the highest OCV value, followed by 2, 4 and 8 M. This trend is strongly related to the fact that the methanol crossover through the membrane becomes increasingly severe with an increase in methanol concentration, thus decreasing the methanol utilisation efficiency [8,21]. Evidently, when a higher methanol concentration is used, a larger amount of methanol is oxidised at the cathode, lead-

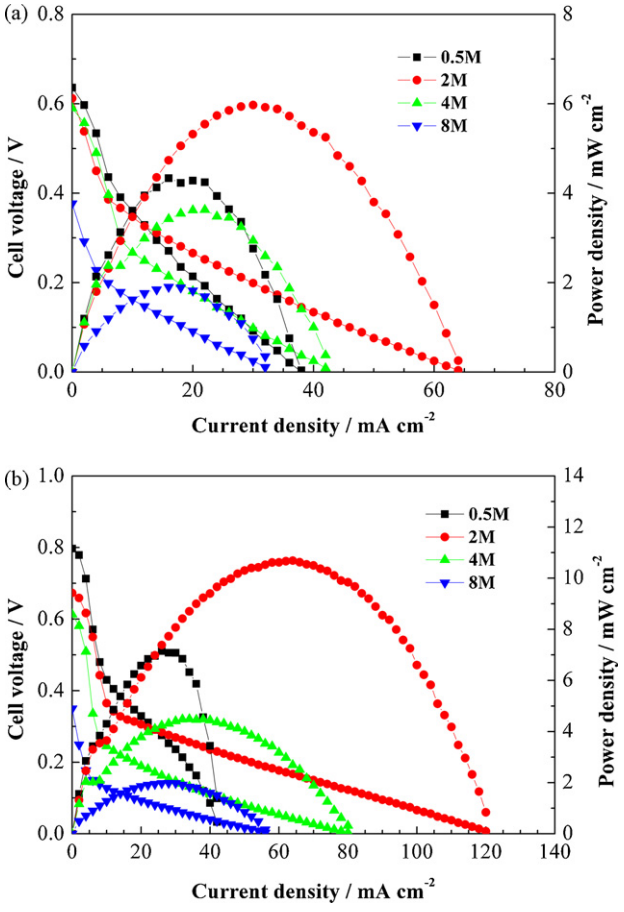

Fig. 13. Performance comparison of the passive DMFC with Nafion 117 membrane at different methanol concentrations: (a) CHA-2 and HPDL; (b) CHA-2 and NBDL.

ing to a higher mixed potential. This pulls down the OCV severely. Nonetheless, the 2 M methanol solution exhibits the best cell performance with the highest power output. It is commonly known that in the case of a passive DMFC, the methanol delivery is mostly driven by a spontaneous concentration gradient [21]. In this situation, a lower methanol concentration cannot provide enough reactant to the catalyst sites due to the mass transfer limitation, while a higher concentration also tends to harm the cell performance as a result of massive methanol crossover. Thus, a moderate methanol concentration of 2 M helps to achieve the optimal cell performance by more efficiently utilising the methanol. Moreover, it is noted that the 0.5 M methanol solution reduces the cell voltage steeply due to great concentration polarisation, in spite of higher maximum power densities compared to 4 and 8 M methanol solutions. It is also worth noting that the relatively high methanol concentrations, e.g. 4 and 8 M, do not enhance cell performance through increased operating temperature caused by heat produced from the exothermic reaction. This fact demonstrates that the effect of the released reaction heat is very limited or even negligible under ambient operating condition. This is different from claims made by some other groups [10,22]. To conclude the above analyses, the 2 M methanol solution is the preferred fuel for optimal performance in a passive DMFC system.

4. Conclusions

Three structural factors were selected for a comparative study of their effects on the performance of a passive air-breathing DMFC: (1) two different open ratios of the current collector; (2) two different assembly methods of the diffusion layer; and (3) three membrane types with different thickness. The interrelations and interactions among these factors were taken into account.

- The open ratio of the current collector has dual effects on cell performance for the DMFC. On one hand, a higher open ratio not only provides a larger area for mass transfer passage, but also facilitates the removal of the produced gas bubbles and residual water. On the other hand, a higher open ratio tends to result in a higher methanol permeation rate and triggers severe methanol crossover, reducing the methanol utilisation efficiency and the cell performance.
- The assembly method of the diffusion layer also exerts an enormous influence on the cell performance. When the DL is hot-pressed, it increases the mass transfer resistance due to its dense structure. This mitigates the methanol permeation but does not aid in the removal of the CO_2 bubbles and accumulated water. When the DL is assembled in the non-bonded form, it allows a higher methanol permeation rate, which may cause serious methanol crossover although it provides a buffer area to help the products leave the fuel cell efficiently.
- The membrane thickness mainly impacts the amount of methanol and water crossover fluxes. A thicker membrane helps obtain a lower methanol crossover rate and higher methanol utilisation efficiency, but also possibly depresses cell performance due to higher mass transfer resistance. Nafion 117 is preferable in the passive air-breathing DMFC to achieve a better overall performance.
- The above factors together affect the cell performance significantly. In this contribution, the maximum power density of 10.7 mW cm^{-2} is obtained with the combination of CHA-2 and NBDL when Nafion 117 is applied. The combination of CHA-1 and HPDL also exhibits an acceptable performance.
- The open circuit voltage increases with the decrease in methanol concentration. An optimum value for the methanol concentration exists: in this study, the 2 M methanol solution yields the best cell performance because of optimal methanol feeding and utilisation.

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