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Experimental results on the direct electrochemical oxidation of methanol in PEM fuel cells[†]

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Abstract

The cell performance of direct methanol fuel cells (DMFC) is 0.5 V at 0.5 A cm^{-2} under high pressure oxygen operation (3 bar abs.) at 110 °C. However, high oxygen pressure operation at high temperatures is only useful in special market niches. Therefore, our work has now focused on air operation of a DMFC under low pressure (up to 1.5 bar abs.). At present, a power density of more than 100 mW cm^{-2} can be achieved at 0.5 V on air operation at 110 °C. These measurements were carried out in single cells with an electrode area of 3 cm^2 and the air stoichiometry only amounted to 10. The effects of methanol concentration and temperature on the anode performance were studied by pseudo half cell measurements and the results are presented together with their impact on the cell voltage. A cell design with an electrode area of 550 cm^2, which is appropriate for assembling a DMFC stack, was tested. A three-celled stack based on this design revealed nearly the same power densities as in the small experimental cells at low air excess pressure and the voltage–current curves for the three cells were almost identical. At 110 °C a power output of 165 W at a stack voltage of 1.5 V can be obtained in the air mode.

1. Introduction

The direct methanol fuel cell (DMFC) is an electrochemical power source based on a simple principle, that is, the direct electrochemical oxidation of methanol to carbon dioxide on the surface of noble metal electrodes [1, 2]. At the cathode the reduction of oxygen (from air) forms water and therefore carbon dioxide and water are the only byproducts produced. The concept is based on a proton exchange membrane as electrolyte, which simultaneously acts as a barrier between the feed reactants (methanol and oxygen/air).

Methanol, as a liquid fuel, is available in large quantities, is easy to handle and relatively easy to distribute. It can also be converted to hydrogen by a fuel processor [3, 4] which would be the ideal fuel for polymer electrolyte fuel cells (PEMFC), but only at the expense of the generation of further pollutants like carbon monoxide, nitric oxides and methane.

In principle, the DMFC system is less complicated than the hydrogen-fuelled PEMFC + fuel processor system, as it needs less components. Reformer, catalytic burner and CO-clean up are not necessary. High temperature processes at several hundred degrees celcius, as in a reformer, can be avoided. The DMFC needs no additional external humidification of gases, since a liquid solution is supplied to the anode keeping the membrane wet. Consequently, the costs for the peripherals are estimated to be lower for a DMFC system than for a hydrogen PEMFC + fuel processor.

On the other hand, there are distinct disadvantages of the DMFC. The cell voltage, hence the efficiency and the power density, are low compared to the hydrogen PEMFC. The relative low power density might be the main disadvantage of the DMFC system. Furthermore, methanol may permeate through the membrane to the cathode [5] and interact with that electrode. Therefore, a loss of the cell voltage occurs, as the cathode potential is decreased [6]. Moreover, the diffusion of methanol to the cathode leads to a loss of fuel and therefore to reduced faradaic efficiency. The water and methanol crossover causes comparative high air stoichiometries. Otherwise, a sufficient cathode performance cannot be ensured. These issues lead to costs for the DMFC stack being higher than for a H_2-fuelled stack. But the DMFC will be competitive if the savings on components compensate for the additional expenses for the stack.

Recently, much effort was made in improving the power density [7–12] but little work has been done in the construction and operation of DMFC short stacks with electrode areas of technical interest [13, 14]. The latter seems to be necessary in order to gain experience in

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operating a DMFC system [8] and to realize the tasks for engineering which will arise with larger systems [15, 16]. In this paper we report results of fundamental experiments with lab-scale cells, as well as experiments with a 550 cm^2 DMFC, which indicate the possibility of scaling up the electrode area without performance loss.

2. Experimental details

The DMFC used in this study was assembled in the conventional way with a Nafion®117 membrane as the polymer electrolyte. The membrane electrode assemblies (MEAs) were prepared by Johnson Matthey. The cathode was constituted from Pt-black with a catalyst loading of about 4 mg cm^{-2}. A high surface area Pt–Ru alloy supported on carbon was used as anode catalyst and the noble metal content of the anode was 1.3 mg PtRu cm^{-2}. Both catalyst materials were developed by Johnson Matthey. Ru has to be used as a second catalyst component, since the methanol oxidation reaction proceeds through the formation of CO as an intermediate, which strongly adsorbs on the Pt surface [1, 17]. Ru reduces the overpotential for CO oxidation and thus considerably increases the catalytic activity of pure Pt [18].

Old data, which are shown in Figure 2 for comparison, were obtained using either an in house prepared Pt–Ru catalyst or PtRu from Johnson Matthey, both being pure unsupported metal catalysts. The corresponding MEAs were also prepared in house.

Some experiments reported by our group [19] and by others [20] in the past were performed with a gaseous fuel supply at the anode. In contrast, our actual operating concept uses liquid methanol-water mixtures. Thus, the polymer electrolyte can be kept at a high level of humidification ensuring good membrane conductivity.

An experimental method called the pseudo half-cell measurement was used for the characterization of the anode performance. An MEA identical to that used for the single cell DMFC studies was mounted in the fuel cell hardware. The anode and the anode reaction remained unchanged, but the cathode was constantly flushed with hydrogen (Figure 1). Thus, the oxygen reduction electrode was replaced by the nearly nonpolarizable hydrogen electrode with an almost constant potential. The electrode reaction taking place at this cathode is the reduction of hydrogen ions, which are transported through the membrane.

Since the combination of these electrode reactions does not lead to a spontaneous overall reaction, the processes are driven by a galvanostat instead of the electronic load which is used for the DMFC experiments. The resulting voltage–current curve represents the anode polarization under load.

Two different cell designs were used in this study. Fundamental experiments were performed using experimental cells with an electrode area of 3 cm^2. This cell design is easy to handle and allows a quick and frequent exchange of the MEA. It is applied to material testing, MEA characterization and pseudo half cell experiments (Section 3.1). A much larger electrode area is required for the construction of a demonstration cell in the 0.5–1 kW range. Therefore, we tested another cell design with an electrode area of 550 cm^2 per single cell. The results for a three cell stack of this design will be shown in Section 3.2.

3. Results and discussion

3.1. *3 cm^2 cell*

Early work on the DMFC focused on high pressure oxygen operation at high temperatures [11, 19]. The cell performance was characterized by a cell voltage of 500 mV at a current density of more than 320 mA cm^{-2} which corresponded to a power density of 160 mW cm^{-2}. The maximum power density was more than 250 mW cm^{-2} at 350 mV. Today, we attain 500 mA cm^{-2} at 0.5 V resulting in a power density of 250 mW cm^{-2}. The maximum power density which can be achieved is more than 380 mW cm^{-2}, but then the cell voltage is only 350 mV (Figure 2).

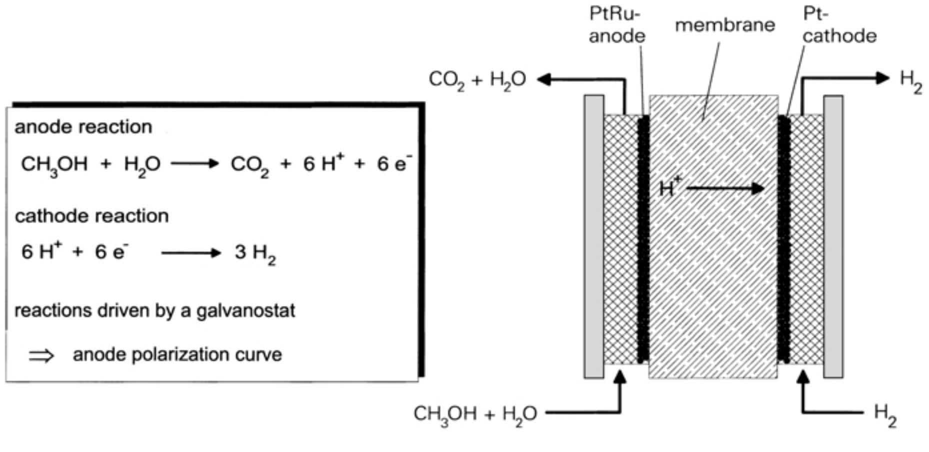

Fig. 1. Schematic principle of the pseudo half cell measurements used for anode characterization.

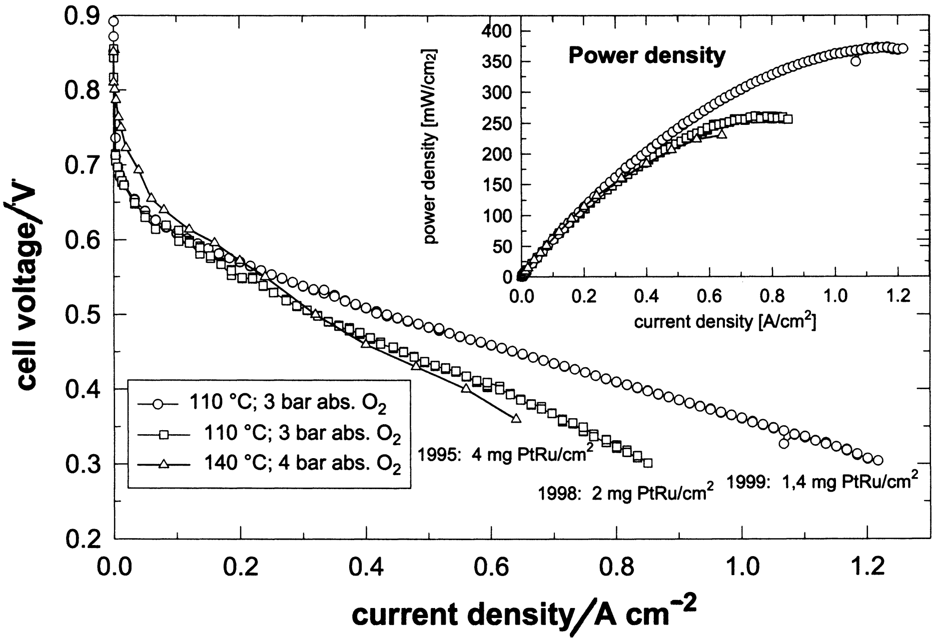

Fig. 2. Voltage–current curves and power density plots (insert) of a 3 cm^2 DMFC on oxygen operation.

Much higher cell performance is now obtained with less drastic experimental conditions. Both the temperature and the pressure have been decreased significantly and the noble metal loading on the anode is reduced to about one third. This illustrates the progress which was made during the last years by the development of new, more active Pt–Ru catalysts and especially by the optimization of the electrode structure.

The performance of the DMFC depends very much on the concentration of the methanol solution fed to the anode. At low current densities the cell voltage increases by about 20–30 mV if the methanol concentration is decreased from 1 M to 0.5 M (Figure 3(a)). The amount of methanol permeating to the cathode is reduced due to the lower concentration and thus the extent of the mixed potential is also reduced. This results in a higher cell voltage, since the anode performance is not significantly affected by the reduced concentration (Figure 3(b)).

In contrast, the highest current densities can only be realized, if a sufficiently high methanol concentration is supplied to the anode (Figure 3(a)). The anode polarization curves clearly indicate a diffusion limitation at comparative low current densities if the methanol concentration is as low as 0.4 and 0.5 M, respectively (Figure 3(b)). In particular, the effect is pronounced at the highest current densities where the methanol diffusion in the pore structure of the electrode becomes rate determining. The curves show a steep increase, which is indicative of diffusion control. But the polarization at high currents is reduced considerably with 0.75 M solution and decreases further with 1 M. At high currents most of the methanol is oxidized at the anode. Hence, the amount diffusing to the cathode is minimized and the cathode poisoning is less pronounced even at high methanol concentrations. Therefore, this improvement of the anode performance at high current densities is not compensated by losses at the cathode and the

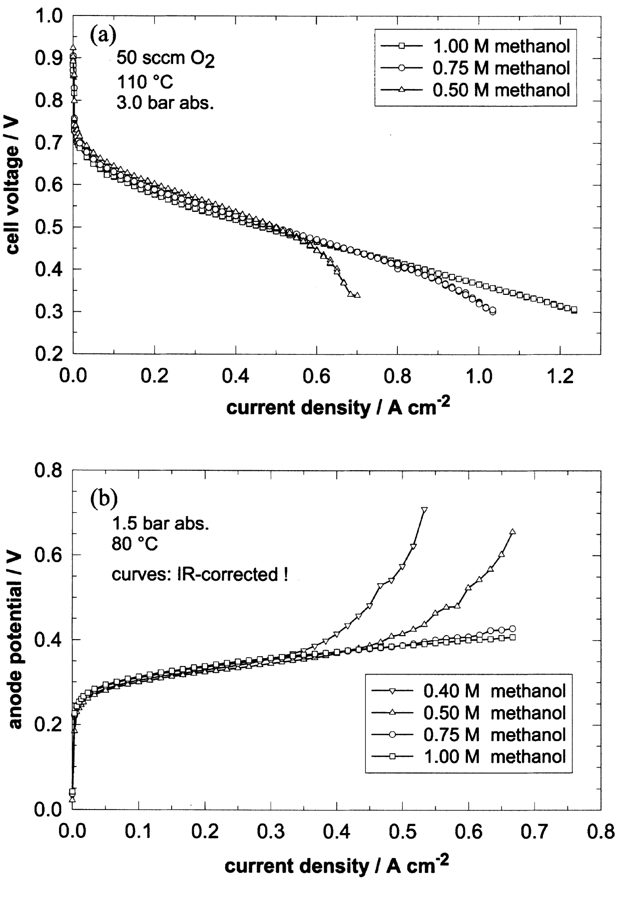

Fig. 3. Influence of the methanol concentration on (a) the cell voltage under oxygen operation and (b) the anode polarization.

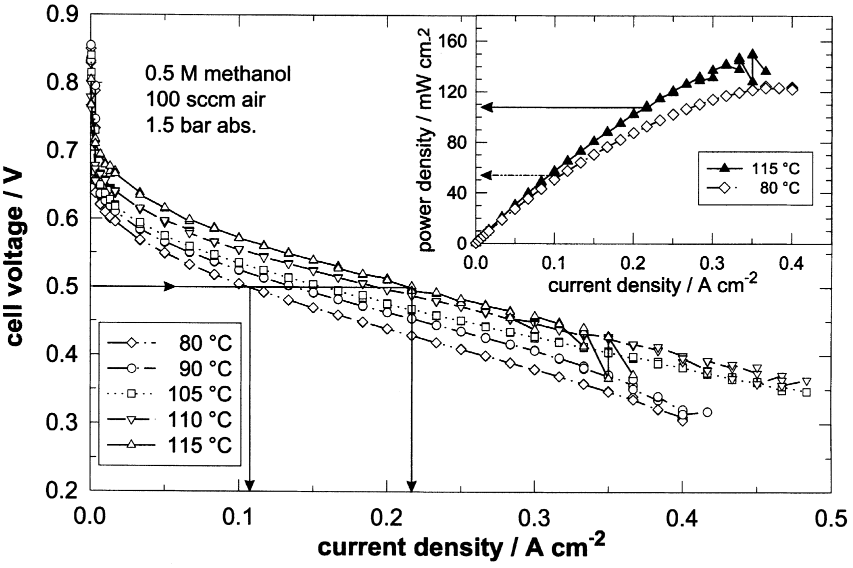

Fig. 4. Voltage–current curves and power density plots (insert) of a 3 cm^2 DMFC on air operation at different temperatures. Arrows in insert indicate the power density at 0.5 V at 80 °C and 115 °C, respectively.

effect is reflected in the increase in cell voltage in the single cell experiments.

Today, the main objective is to supply air instead of pure oxygen to the cathode and to operate a DMFC at low pressures, usually 1.5 bar abs. In Figure 4 voltage–current curves are shown, which were measured at experimental conditions meeting the present requirements. The pressure was 1.5 bar, air was supplied to the cathode with a stoichiometric ratio of 10 at 200 mA cm^{-2}. The temperature was varied between 80 and 115 °C. The power density plots for the lowest and highest temperature are shown in the small figure. It can be seen clearly, that there is a strong influence of the temperature on the cell performance.

Since the cell voltage is directly related to the efficiency of the fuel cell, we suppose 0.5 V to be the lowest reasonable voltage for economic operation of a DMFC. At that voltage we obtain a current density slightly higher than 100 mA cm^{-2} at a cell temperature of 80 °C and thus the power density amounts to 50 mW cm^{-2}. If the temperature is raised, the performance continuously increases up to 115 °C, where we obtain almost 220 mA cm^{-2} and this results in a power density of nearly 110 mW cm^{-2}, more than twice the value at 80 °C. The maximum power density is around 150 mW cm^{-2}, but this corresponds to a cell voltage of only 430 mV. A further increase in temperature beyond 115 °C did not result in an additional improvement of the cell performance, since the pressure was kept constant.

The effect of elevated temperatures can be seen in more detail in Figure 5. The anode potential decreases considerably with increasing temperature, since the kinetics of the CO oxidation are more favourable at higher temperatures and thus the overpotential is reduced.

At a current density of 200 mA cm^{-2} the polarization is reduced by 75 mV to 270 mV if the temperature is raised from 80 to 110 °C. This improvement in anode potential is larger than the cell voltage increase measured with the DMFC configuration at the same current density and in the same temperature interval. The DMFC performance increases by only 50 mV. The reason for this behavior is the deterioration in cathode performance, which suffers from enhanced methanol and water crossover and from higher water partial pressure at elevated temperatures. Therefore, a part of the improvement at the anode is compensated by losses at the cathode, leading to the cell voltage improvement being smaller than expected. The worse cathode performance at high temperatures is also reflected in the voltage–current curves, where considerable scattering occurs at the highest currents (Figure 4).

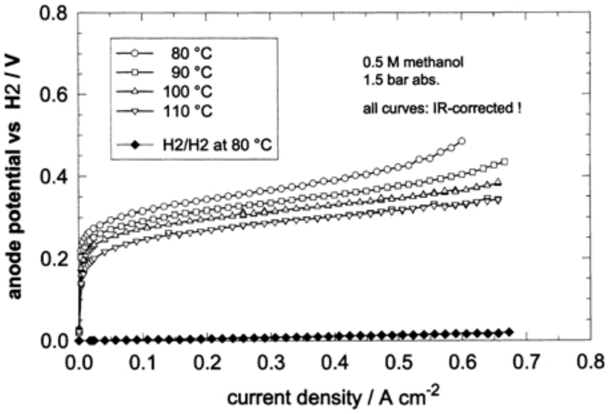

Fig. 5. Influence of the temperature on the DMFC anode polarization on air operation. The straight line (bottom) represents the cell voltage of a symmetrical arrangement (two hydrogen electrodes) and indicates a neglectable contribution of a single hydrogen electrode to the pseudo half-cell measurements.

In an additional experiment both electrodes were fed with hydrogen. In this case one was working as a hydrogen oxidation electrode and the second as a hydrogen evolution electrode. The voltage–current curve for a symmetrical cell (Figure 5) showed a tiny polarization of the two hydrogen electrodes and therefore indicates a negligible influence of a single hydrogen electrode on the pseudo half cell measurements. Consequently, the curves in Figures 3(b) and 5 characterize methanol oxidation.

3.2. *550 cm^2 cell*

In Figure 6 the single voltage–current curves for the three cells of the stack are shown for air operation. The experimental conditions were 110 °C and 1.5 bar abs. The performance curves of all cells are in reasonable agreement with each other and, consequently, the different cells in the stack are homogeneously supplied with reactants.

On average, the target cell voltage of 0.5 V is achieved at 175 mA cm^{-2}, the air stoichiometric ratio being 6. This corresponds to an average power density of 87 mW cm^{-2}. At this single cell voltage the overall power output from the stack was 144 W (corresponding to 48 W per cell), whereas the maximum power output was 185 W, but then the mean single cell voltage dropped to 410 mV.

The power density of the DMFC stack depends very much on the air flow rate. On tripling it, the average performance at 0.5 V per cell increases from 155 to 200 mA cm^{-2} and hence the overall power rises from 130 to 165 W (Figure 7).

At a stoichiometry of 11 (at 200 mA cm^{-2}), the power density was 100 mW cm^{-2} and consequently the 550 cm^2 stack approaches closely to the performance of the 3 cm^2 cell, which was also operated at a similar stoichiometry

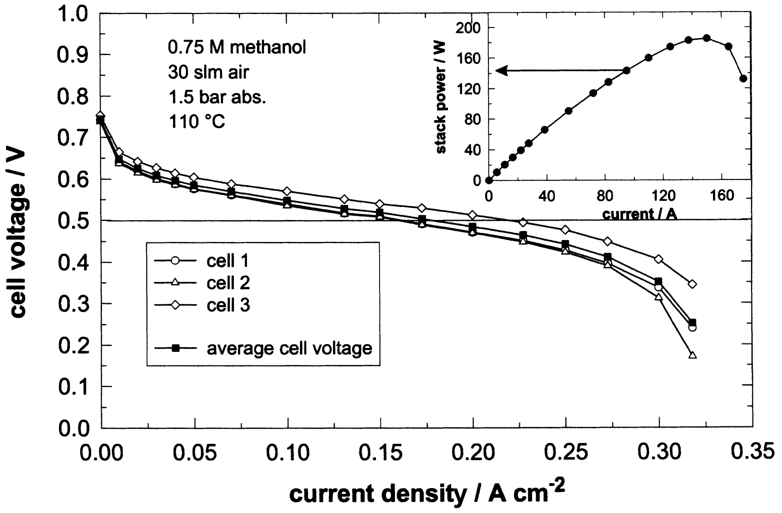

Fig. 6. Voltage–current curves of the cells in a three cell 550 cm^2 stack on air operation. Arrow in insert indicates the stack power output at an average cell voltage of 0.5 V.

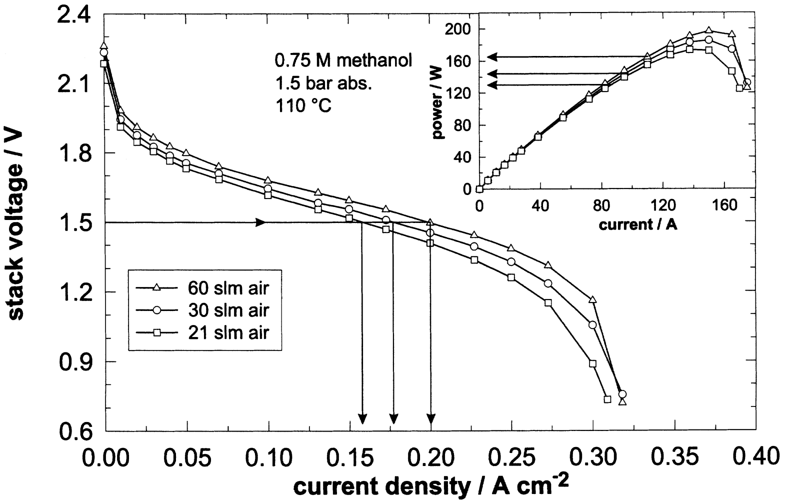

Fig. 7. Influence of the air flow rate on the performance of the three cell 550 cm^2 stack. Arrows in insert indicate the stack power output at an average cell voltage of 0.5 V.

of 10. This is considered as indicative of successful scale-up both of the MEA and of the cell design.

We can conclude that the cell design including the manifold and the flow fields is appropriate for assembling a multicelled DMFC stack in the power output range of 1 kW. The loss of performance at the lower, but more practical, flow rates is due to excessive flooding of the cathode structure. This illustrates once more the need for a new DMFC specific membrane, which is essential for the economic operation of such a DMFC stack. Although the air stoichiometry has been significantly reduced over recent years, it is still too high for efficient stack operation.

4. Conclusion

The DMFC performance is characterized by a power density of about 250 mW cm^{-2} at 500 mV on high pressure oxygen operation. On air operation at low pressure the power density amounts to more than 100 mW cm^{-2} at the same cell voltage with the noble metal loading being 1.3 mg PtRu cm^{-2} on the anode and 4 mg Pt cm^{-2} on the cathode.

In the 550 cm^2 cell nearly the same power density as in the small experimental cells, is obtained. The three-cell stack revealed a performance of 144 W at 1.5 V at 110 °C and a pressure of 1.5 bar abs., if the air stoichiometry is only 6. The performance increased to 165 W at higher, but impractical, stoichiometries.

The power density of the DMFC has been considerably increased in recent years, but it must be further increased by future improvements of the anode catalyst activity and of the electrode structure in order to decrease the stack costs. In parallel, the air stoichiometry was significantly reduced, but it is still too high for practical systems in terms of energy losses for air compression. The high flow rates are required to remove the large amounts of water and methanol diffusing through the Nafion®117 membrane. Therefore, the development of a specific DMFC membrane with a low methanol and water permeation and the optimization of the electrode structure will be the key issues for the development of a realistic DMFC system. These parameters could increase the faradaic efficiency and reduce the poisoning and flooding of the cathode and thus lead to an increase in cell voltage and to a reduction in air stoichiometry. The latter is inevitable for a technical application.

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