

45% Cell Efficiency in DMFCs via Process Engineering▲

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Received December 18, 2019; accepted June 07, 2020; published online August 03, 2020

Abstract

Methanol is a convenient liquid fuel for fuel cells, but is not converted as efficiently into electrical energy as hydrogen. This is due to the slower reaction of methanol at the anode as well as to methanol permeation.

When optimizing the direct methanol fuel cell (DMFC) process, methanol concentration and flow rate, current density and air flow rate must also be taken into account. A high methanol concentration facilitates dynamic operation up to high current densities, but also leads to high methanol permeation. The air flow rate must be adjusted so that the cooling effect of evaporating water is balanced by the heat produced in the cell. Therefore, a cell with low permeation must

be operated at low air flow rates to achieve autothermal operation at elevated temperatures, which can in turn reduce cell performance. For each current density, there is an optimum amount of methanol feed.

In this paper, we show how these effects have to be balanced using air-flow rates calculated to ensure thermal equilibrium. It is possible to achieve electrical cell efficiencies of up to 44% in a self-heating DMFC. Another small increase in efficiency can be achieved by using humidified air at the cathode.

Keywords: Cell Efficiency, Direct Methanol Fuel Cell, Electrochemistry, Energy Conversion, Faradaic Efficiency, Fuel Cells, Methanol Permeation


1 Introduction

Direct methanol fuel cells (DMFCs) have reached a state of technological readiness where they can be used for several different applications, such as light traction [1], uninterruptable power supply [2] and leisure equipment [3]. However, the cost of power from DMFC systems is still relatively high. This is only partially due to their investment costs. A significant part of the total cost of ownership is related to the cost of methanol [2]. This is due to the low efficiency of current DMFCs of generally between 20% and 30%. Our aim here is to increase the total efficiency of a DMFC system to 35%, which requires, at an assumed system efficiency of 80%, a cell efficiency of 43.75%.

While efficiency has a direct influence on total cost of ownership and energy density of the system, power density is also relevant for DMFC systems. Depending on the requirements for a specific application, some of these properties will be more relevant than others, so a suitable system must be designed. Systems with a power output of more than a couple of Watts are usually designed as active systems. That means that a dilute methanol solution is recirculated through the stack and replenished with pure methanol from a tank as methanol is consumed and air is pumped through the stack. Passive systems, where neat methanol is added and diffuses to the membrane electrode assembly (MEA) surface, air is provided by

▲ Paper presented at the 23rd EFCF Conference “Low-Temperature Fuel Cells, Electrolyzers, H₂-Processing Forum” (EFCF2019), 2–5 July 2019 held in Lucerne, Switzerland. Organized by the European Fuel Cell Forum www.efcf.com

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diffusion and convection are more suitable for applications with low power requirements which need to be very small.

The cell efficiency of a DMFC is defined as the electrical power output of the cell divided by the lower heating value of the methanol consumed by the cell. Most publications focus only on a single aspect of efficiency, like cell voltage [4–8], methanol permeation [4, 5, 9–12], or system efficiency [13]. In the literature, a number of publications determining cell efficiency values can be found, but the topic has not been studied systematically. Seo et al. investigated the effect of different operating parameters like temperature, methanol concentration, flow rates of air and methanol and pressure, but did not take into account whether the cells would reach the temperature without external heating. However, efficiencies of up to 27% were achieved [14]. Casalegno et al. studied how these parameters influence methanol permeation and obtained similar results with efficiencies of up to 24% [15]. Meanwhile, Chiu et al. developed a semi-empirical model to determine DMFC efficiency. The maximum efficiency calculated by the model based on their experiments is 32% of the higher heating value of methanol, which is 36% of the lower heating value [16]. A similar efficiency of 35% was experimentally obtained by Park et al. in a self-heating DMFC stack [17]. Yeh et al. compared efficiency data from a 3-cell stack, fed with heated methanol and a self-heating, 26-cell stack [18]. They found that the efficiency of the heated stack reaches up to 38% (not considering the energy needed to heat up the methanol), while the self-heating stack achieved only 27% efficiency. The main difference in operating parameters was in the cathode air flow rate, which was reduced from $28 \text{ mL cm}^{-2} \text{ min}^{-1}$ to $8 \text{ mL cm}^{-2} \text{ min}^{-1}$, in order to keep the stack in a temperature range from 60°C to 70°C . They also studied the change in efficiency during a test of 4,000 operating hours. During this time, the efficiency degraded to 27% in the heated 3-cell stack and to 17% in the self-heating, 26-cell stack. Dohle et al. discussed the efficiency of a pressurized system, finding that high cell efficiencies in a pressurized system lead to a lower system efficiency, due to energy consumed by the compressor [19]. Gottesfeld showed that stack conversion efficiencies of 35% can be achieved by controlling methanol feed so that a faradaic efficiency of 90% is achieved [20]. Gao et al. estimate cell efficiency from a model they do not describe in detail to be 38% [21], while assuming the system's efficiency to be 82%. In their review of DMFCs [22], Joghee et al. also mention that efficiencies of up to 38% have been experimentally demonstrated in single cells. They assume that efficiencies up to 44% can be reached, if a DMFC is operated at 0.5 V at a faradaic efficiency of 97%.

While these works show the efficiencies actually achieved, Mergel et al. claim [1] that a total system efficiency of 30% must be reached in order for a DMFC to be cost competitive against other technologies. At a system efficiency of 80%, this would require a cell efficiency of 37.5%. This, according to the literature reviewed above, has not been achieved so far, but is regarded as being realistic.

2 Experimental

2.1 Scientific Approach

The highest possible efficiency will be achieved when the amount of methanol fed into the cell is just high enough so that no significant losses due to diffusion limitations occur. This is due to the fact that the oxidation of methanol is zero order in methanol concentration if above 0.01M at the catalyst surface, as shown by Gottesfeld [20] and Vidakovic [23].

If more methanol is fed into the cell, losses due to methanol permeation will increase, while the cell voltage will not significantly increase. The amount of methanol needed will, of course, depend on the current density and can be limited by the methanol concentration in the feed stream and its flow rate. It is expected that better results can be achieved by using a low concentration at a high flow rate because in this way the methanol concentration will remain relatively constant from the inlet to the outlet. When using a high concentration at a low flow rate, methanol concentration will change significantly from the inlet to the outlet, so that the conditions will not be optimal at all positions of the cell. Similar considerations were discussed by Gottesfeld in a review on "Design concepts and durability challenges for mini fuel cells" [20]. He showed that methanol loss can be reduced to less than 10%, by using low stoichiometric flow rates.

In order to ensure that the cell can actually be operated in a DMFC system, it must be considered that the cell will assume an equilibrium temperature, mainly depending on the evaporation of water affected by the air flow rate. In order to achieve good performance and avoid premature aging, the operating temperature chosen was 70°C and the air flow rates were calculated so that thermal equilibrium was achieved at this temperature. As these air flow rates are relatively low, it would be desirable to use higher air flow rates. The evaporation of water at the cathode is the main cooling factor, so higher air flow rates are possible if humidified air is used and thus evaporation is limited.

2.2 Experiments and Calculations

DMFC measurements were performed using a commercial MEA obtained from Johnson Matthey Fuel Cells. These were mounted in a test cell with an active area of $42 \times 42 \text{ mm}^2$. Flow-fields were machined from graphite and had a checkerboard design, with 1 mm as the width and depth of the channels, as well as the width of the lands. The cells were heated in order to compensate for thermal losses from the surfaces, but the operating parameters were chosen so that a larger stack, where surface losses become negligible, would heat itself to the operating temperature.

The cells were operated in a custom-built test rig. Methanol is taken from tanks of 3 molar solution, 0.75 molar solution and pure water by a 3-channel peristaltic pump and mixed in order to obtain the required concentration at the required flow rate. Air was fed into the cell with a mass flow controller and

no back-pressure was used. At the cathode exhaust, water was condensed and the concentration of CO₂ in the dried exhaust air measured. From this, the methanol permeation was calculated, assuming that all permeated methanol is oxidized to CO₂. In order to facilitate the comparison of permeated methanol to methanol used for current generation, the current that could have been generated by the permeated methanol is calculated and the methanol permeation is given in A cm⁻².

In order to ensure that the cell is operated in thermal equilibrium, the processes heating and cooling the cell must be in balance. The cell is heated by having a cell voltage that is lower than the cell voltage corresponding to the higher heating value of methanol and by methanol permeation, which leads to a portion of methanol being oxidized at the cathode and generating only heat. It is cooled by the cathodic air, which enters the cell at room temperature and leaves it at its operating temperature, and by water evaporating at the cathode. As the cell is operated at low air flow rates in order to achieve high cell temperatures, it can be assumed that the air is saturated with water vapor at the cathode exhaust. All measurements presented in this paper were obtained in thermal equilibrium at 70 °C. Current density, methanol concentration and methanol feed rate were chosen to study a certain effect, while the air flow rate was calculated such that the cell is in thermal equilibrium.

Efficiency is defined as the fraction of chemical energy of methanol which is converted into electricity. To calculate the efficiency, the chemical energy of methanol must be defined. In this paper, we use the lower heating value of methanol, as the lower heating value of fuels is frequently used to calculate conversion efficiencies in energy applications. This has also been performed by other authors [1]. From a thermodynamic point of view, it is useful to relate the efficiency to the Gibbs free energy, which has also frequently been undertaken in literature [20, 21]. A third possibility is to use the higher heating value or enthalpy of combustion, which can also be found in literature [16, 22]. The cell voltages for 100% voltage efficiency are $U_{LHV} = 1.10$ V for the lower heating value, $U_{HHV} = 1.25$ V for the higher heating value and $U_G = 1.21$ V for the Gibbs free energy. Therefore, efficiencies based on different energies can easily be converted as follows: $\eta_{HHV} = \eta_{LHV} \times 1.10/1.25$, where η_{HHV} is the efficiency based on the higher heating value and η_{LHV} is the efficiency based on the lower heating value. Furthermore, $\eta_G = \eta_{LHV} \times 1.10/1.21$, where η_G is the efficiency based on Gibbs free energy.

The amount of methanol fed into the cell is always more than the amount necessary to generate the required current. As the methanol solution will be recirculated in a DMFC system, this excess is not lost. The amount of methanol consumed n can be calculated from the current density i and methanol permeation i_p using Faraday's law (Eq. (1)):

$$n = (i + i_p) \times t / (z \times F) \quad (1)$$

where $z = 6$ is the number of electrons per molecule of methanol, F is the Faraday constant and t is the time. As current density and methanol permeation current density are given in A cm⁻² of active cell area, n is obtained in mol per cm² and minute if t is chosen as 60 s. Thus, for a current density of 0.1 A cm⁻² and permeation current density of 0.01 A cm⁻², 0.0114 mmol of methanol per cm² and minute are consumed. Depending on the amount of methanol fed into the cell, this will lead to a more or less significant reduction of methanol concentration from the methanol inlet to methanol outlet of the cell. In Table 1 outlet concentration is calculated for a few operating conditions.

In order to assure operation in thermal equilibrium, the following heating and cooling contributions are considered. Thermal losses from the external surfaces are not considered, as they become very small in a large, well-insulated stack. The stack is heated by the voltage heat contribution Q_V caused by the cell voltage U_{Cell} being lower than the voltage corresponding to the energy of methanol (Eq. (2)), and by the Faradaic heat contribution Q_F caused by permeated methanol being oxidized at the cathode (Eq. (3)).

$$Q_V = i \times (U_{HHV} - U_{cell}) \quad (2)$$

$$Q_F = i_p \times U_{HHV} \quad (3)$$

The cooling contributions are Q_A , caused by cool air entering the cell (Eq. (4)), and Q_W , caused by water evaporating at the cathode (Eq. (5)). Q_A depends on the temperature difference ΔT between the temperature of the air entering the cell and the cell temperature T , the heat capacity of air $c_{P(air)}$, the density of air $\rho_{(air)}$ and the cathodic flow rate CFR of the air entering the cell. Q_W depends on the enthalpy of evaporation

Table 1 Methanol concentration at inlet and outlet for different operating conditions.

c (inlet) / mol L ⁻¹	Methanol flow rate / mL cm ⁻² min ⁻¹	Methanol feed rate / mmol cm ⁻² min ⁻¹	Current density / A cm ⁻²	Methanol permeation / A cm ⁻²	Methanol consumption / mmol cm ⁻² min ⁻¹	c (outlet) / mol L ⁻¹
1.0	0.055	0.055	0.3	0.009	0.0320	0.42
0.75	0.44	0.33	0.3	0.017	0.0329	0.68
0.5	0.025	0.0125	0.06	0.01	0.0073	0.21
0.25	0.22	0.055	0.06	0.009	0.0072	0.22
0.5	0.015	0.0075	0.048	0.006	0.0056	0.13
0.2	0.22	0.044	0.048	0.007	0.0057	0.17

ΔH_v and the water vapor partial pressure p_{H_2O} on the temperature of the cell. R is the gas constant.

$$Q_A = DT \times c_{P(air)} \times r_{(air)} \times CFR \quad (4)$$

$$Q_W = DH_v \times p_{H_2O} \times CFR_{out} / (R \times T) \quad (5)$$

The cathodic outlet flow CFR_{out} can be calculated as:

$$CFR_{out} = (CFR - V_{Cons} + V_{Gen}) \times 101,325 \text{ Pa} / (101,325 \text{ Pa} - p_{H_2O}) \times T / 273.15 \quad (6)$$

with

$$V_{Cons} = (i + i_p) / (4 \times F) \times (R \times T / 101,325 \text{ Pa}) \times 1,000 \quad (7)$$

$$V_{Gen} = (i_p) / (6 \times F) \times (R \times T / 101,325 \text{ Pa}) \times 1,000 \quad (8)$$

The consumption of oxygen V_{Cons} is caused by the generation of current and methanol permeation, whereas the volume of CO_2 V_{Gen} is only generated in the cathode through the oxidation of the permeated methanol.

It is assumed that the entire methanol which permeates to the cathode is converted into CO_2 and that the air leaving the cathode is saturated with water vapor at the temperature of the cell. These assumptions have been tested and found to be true under the conditions used in this study. Therefore, in Eqs. (2) and (3), U_{HHV} is used, as the evaporation of product water is regarded separately in Eq. (5).

The loss of methanol by evaporation into the anodically generated CO_2 in the gas separator is neglected. We consider this to be part of the system efficiency. Due to the low methanol concentration the methanol vapor pressure is also low. For a concentration of 0.5M, 0.5 mol of methanol are dissolved in 55 mol of water. Even though the vapor pressure of pure methanol is 127,900 Pa, the vapor pressure of the mixture is only 1,150 Pa. That is little over 1% of the amount of CO_2

generated by methanol oxidation at the cathode. For lower concentrations, this value is even lower.

3 Results and Discussion

In order to maximize DMFC efficiency, the amount of methanol fed into the cell must be kept as low as possible so that the fuel cell continues to generate a high cell voltage, but methanol permeation is limited. When the cell was operated with different concentrations of 0.5M to 1.0M methanol and flow rates between $0.055 \text{ mL cm}^{-2} \text{ min}^{-1}$ and $0.44 \text{ mL cm}^{-2} \text{ min}^{-1}$, the cell voltage at low current densities was highest for low concentrations and low flow-rates (Figure 1). For high current densities, in contrast, the highest cell voltages were achieved with higher concentrations and flow rates.

The methanol permeation is, as expected, lower for lower methanol concentrations. With increasing current density, the effect of the flow rate increases and low flow rates lead to lower permeation (Figure 2). This can be used as an alternative for reducing the concentration. At a current density of 0.3 A cm^{-2} methanol permeation for 1.0 M methanol and the lowest flow rate is lower than for 0.75 M methanol and higher flow rates. This is due to depletion of methanol in the cell. At 1.0M methanol and a flow rate of $0.055 \text{ mL cm}^{-2} \text{ min}^{-1}$, $0.055 \text{ mmol cm}^{-2} \text{ min}^{-1}$ are fed into the cell, while at 0.75M methanol and $0.44 \text{ mL cm}^{-2} \text{ min}^{-1}$, $0.33 \text{ mmol cm}^{-2} \text{ min}^{-1}$ are fed into the cell. Of this amount, $0.032 \text{ mmol cm}^{-2} \text{ min}^{-1}$ are consumed, so in the first case 58% of the methanol is consumed and the methanol concentration at the outlet is reduced to 0.42M. In the second case, less than 10% are consumed and the methanol concentration at the outlet is 0.68M (see Table 1). Thus, a combination of inlet and outlet concentration must be considered in future discussions. In all cases, when methanol permeation falls below 0.01 A cm^{-2} , cell voltage decreases significantly. Apparently, under these conditions the methanol concentration at the outlet is too low for higher current densities. As stated above, this limitation is generally not due to an increased overpotential at the catalyst for low concentrations

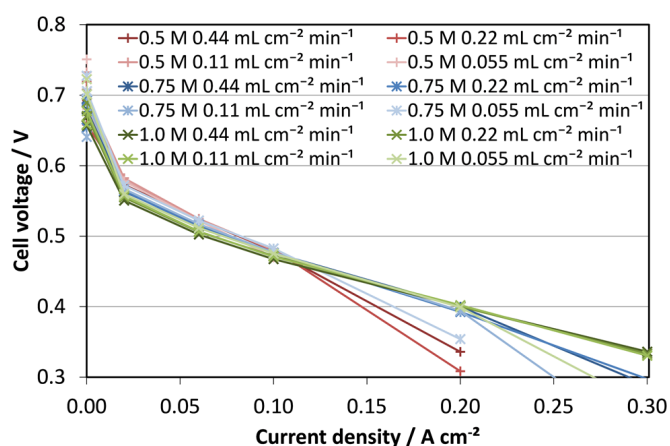


Fig. 1 Current-voltage curves for different methanol concentrations and flow-rates.

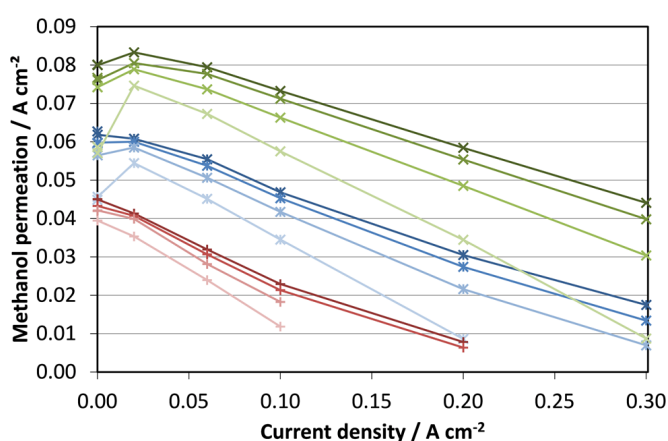


Fig. 2 Methanol permeation curves for the same methanol concentrations and flow-rates as in Figure 1.

but due to diffusion limitations in the gas diffusion layer and catalyst layer of the anode [20].

Therefore, it is necessary to adjust the methanol feed to the current density required from the DMFC. In Figure 3, the efficiency is plotted over the power density for a variety of different operating conditions, as is shown in Figure 1. To facilitate interpretation of the results, points obtained at the same current density are connected to lines of a certain color.

The general shape of these curves is shown in Figure 4 for a current density of 0.2 A cm^{-2} . At the highest methanol feed rates (flow rate and concentration), the power density is more or less constant, while the efficiency increases when decreasing the methanol feed. Under these operating conditions, cell voltage does not change significantly with methanol feed, while methanol permeation decreases with decreasing methanol feed and therefore faradaic efficiency increases. This is only true up to a certain point though. If the methanol feed is further decreased, the cell voltage and therefore the power density will decrease. The efficiency decreases at the same time, because under these operating conditions methanol permeation is already so low that faradaic efficiency can no longer significantly increase and the voltage efficiency decreases. It appears that the methanol feed is now so low that methanol diffusion resistance to the catalyst surface leads to an additional loss in voltage. While this shape is fully formed for 0.2 A cm^{-2} , for some higher or lower current densities, only part of this can be seen. To see the full shape, it would be necessary to further increase or decrease the methanol feed. The best operating condition for high efficiency at high power output is the methanol feed at the point where efficiency is highest and power density is close to its maximum.

In Figure 5, the same data are plotted, while the lines connect data points obtained at the same methanol feed. It can be seen that for the lowest concentrations and flow rates, only a limited power density can be obtained. For higher concentrations and flow rates, higher power densities can be achieved. It is also possible to operate the DMFC at high concentrations and high flow rates when using only low power densities.

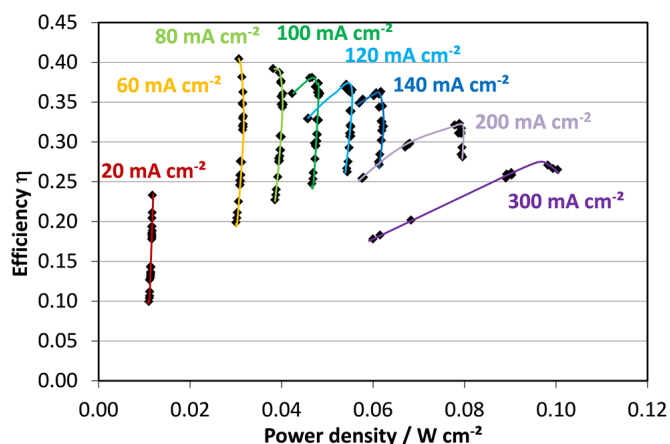


Fig. 3 Efficiency over power density for concentrations and flow rates as in Figure 1. Data obtained at the same current density are connected by lines.

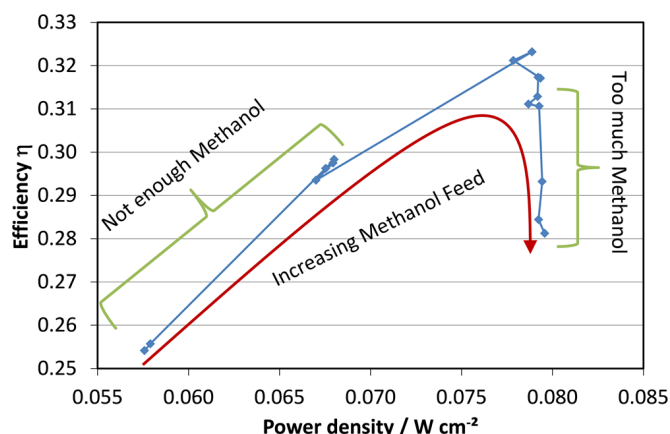


Fig. 4 Efficiency over power density at 0.2 A cm^{-2} with change in the methanol feed.

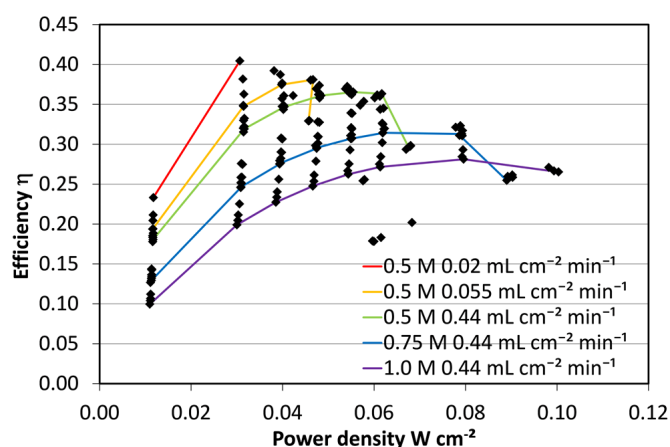


Fig. 5 Efficiency over power density as in Figure 3. Data obtained at the same methanol concentration and flow rate are connected by lines.

Under these conditions, however, the efficiency of the DMFC is much lower than it could be if it was operated with an appropriate methanol feed.

To obtain the best possible efficiency, the methanol feed can be adjusted by changing the methanol flow rate at constant methanol concentrations or methanol concentrations can be adjusted at constant methanol flow rates. In Figure 6, it is shown that when adjusting the methanol flow rate at 0.3 M methanol concentration, the maximum efficiency shifts to lower current densities and higher values when the flow rate is decreased. A similar effect can be observed when the methanol concentration is lowered at a constant flow rate, as shown in Figure 7.

It remains to be determined whether reducing the flow rate or reducing the methanol concentration is the better way to increase DMFC; this is shown in Figure 8. Two pairs of operating parameters for which the highest efficiency was obtained under similar current densities were tested. In one case, the methanol concentration was 0.5 M and the flow rate was decreased to $0.025 \text{ mL cm}^{-2} \text{ min}^{-1}$ and $0.015 \text{ mL cm}^{-2} \text{ min}^{-1}$, respectively, while in the other case the flow rate was kept at $0.22 \text{ mL cm}^{-2} \text{ min}^{-1}$ and the methanol concentration was

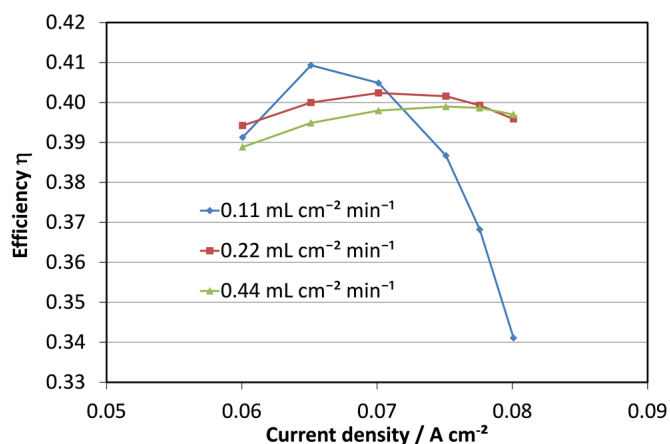


Fig. 6 Efficiency over the current density for different flow rates of 0.3M methanol.

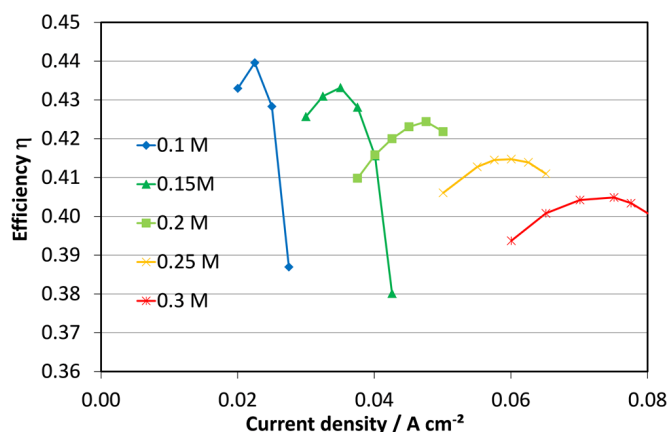


Fig. 7 Efficiency over current density for low concentrations and $0.22 \text{ mL cm}^{-2} \text{ min}^{-1}$ flow rate.

decreased to 0.25M and 0.2M. No big difference in current density and efficiency was observed at the efficiency maximum for the moderately reduced concentration or flow rate, as outlet concentration is similar (see Table 1), while for the lowest concentration and flow rate, both the efficiency and current density at maximum efficiency were higher when the methanol concentration was reduced. This was to be expected, because with higher flow rates it is possible to feed more methanol into the cell without increasing permeation so much that the efficiency is decreased. For the lowest concentration (0.2M methanol at $0.22 \text{ mL cm}^{-2} \text{ min}^{-1}$) $0.044 \text{ mmol cm}^{-2} \text{ min}^{-1}$ of methanol were fed into the cell, whereas for the lowest flow rate ($0.015 \text{ mL cm}^{-2} \text{ min}^{-1}$ of 0.5M methanol), only $0.0075 \text{ mmol cm}^{-2} \text{ min}^{-1}$ were provided; less than 20%. As shown in Table 1, this leads to an outlet concentration of 0.13M or 0.17M, respectively. As a consequence, the methanol concentration is more homogeneously distributed over the surface of the MEA for the lowest concentration and the operating conditions can be more homogeneous. As it has been shown that the highest current density and efficiency are obtained across a relatively narrow range of operating parameters, an inhomogeneous distribution of operating parameters

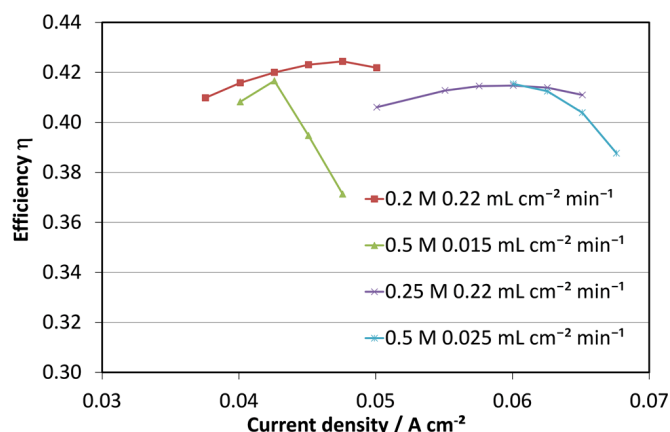


Fig. 8 Efficiency over current density for low concentrations and low flow rates.

over the cell surface will lead to non-optimal conditions, at least in parts of the cell. Thus, for the lowest methanol concentration, an efficiency of 44% of the lower heating value was obtained. By reducing the methanol feed rate for higher concentrations, high efficiencies can only be obtained by consuming the largest part of the methanol within the cell. As a consequence, increasing the current density is no longer possible, as can be seen from the sharper decay of efficiency with increasing current density for the corresponding curves in Figure 8.

Another point to keep in mind when choosing optimal operating conditions is if highly dynamic operation of the DMFC is required. In this case, the flow rate of the methanol can typically be adjusted more quickly than the methanol concentration. Thus, using a higher concentration and low flow rate will permit the rapid increasing of the flow rate if higher power is required from the DMFC. As DMFC systems are generally hybridized with a battery, this is often not necessary. A sudden increase in power demand can be compensated by the battery until the methanol concentration in the DMFC has been adjusted to a higher value.

When comparing all the data obtained at different operating conditions but always in thermal equilibrium (Figure 9), it

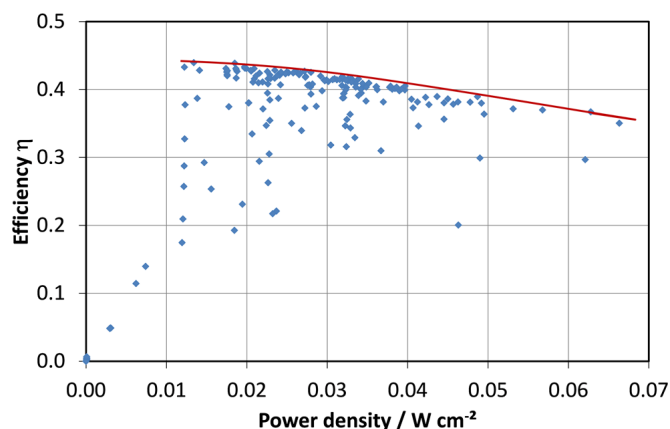


Fig. 9 Efficiency and power density of all auto thermal operating states (line through maxima is a guide for the eye).

becomes clear that there is an upper limit. The efficiency at this upper limit is a function of the power density. It is possible to reach this upper limit if the operating conditions are optimal for a given power density. The operating conditions should be chosen so that this limit will be reached. In order to move beyond it, which is characteristic for each cell, better cells or materials are required.

Another way of moving this limit upwards can be the use of humidified air. By humidifying the air fed into the cathode to a dew point of 61 °C or 65 °C, the air has a relative humidity of 66.7% or 80% at 70 °C. This means that it already contains 2/3 or 4/5 of the water vapor it can take up. Therefore, the air flow rate can be multiplied by 3 or 5, in order to evaporate the same amount of water from the cathode as with the calculated amount of dry air. In Figure 10, the efficiency maxima and power density for several different methanol feed combinations (concentration and flow rate) are plotted for dry and humidified air.

It can be seen from Figure 10 that the highest efficiency, of almost 45%, can be achieved with dry air. Considering the efficiency over power density curve for dry and humidified air, it can be seen that the best results are obtained with dry air for the lowest power densities and with humidified air at higher power densities. In this way, cell efficiencies of above 37.5% can be reached for power densities of more than 50 mW cm⁻².

4 Conclusions

It was shown in this study how it is possible to adjust methanol feed in an auto-thermally operated DMFC to obtain the highest possible efficiency for a given power output. Depending on the required power density, DMFC efficiencies of up to 45% were reached at a power density of 20 mW cm⁻² and 37.5% efficiency was reached at more than 50 mW cm⁻². Assuming a system efficiency of 80%, this will lead to a total efficiency of the DMFC system of 35% or 30%, respectively, reducing DMFC costs by reducing the costs of methanol due to lower methanol consumption at a given power demand.

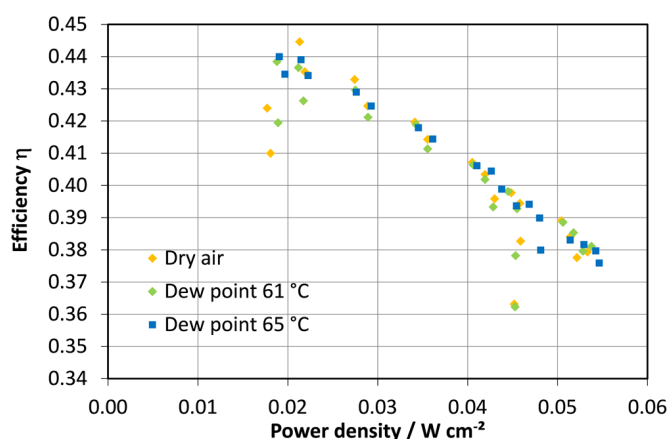


Fig. 10 Highest efficiency for each combination of the methanol concentration and flow rate for dry and humidified air.

The most efficient way to improve efficiency was shown to be to limit the amount of methanol to the amount necessary to generate the required power. In an optimal scenario, the same methanol concentration is available over the entire surface of the MEA and thus the entire cell can be operated homogeneously. Experimentally, this can best be approached by using a relatively low methanol concentration at a high flow rate, so that much more methanol is circulated through the cell than is required for current generation.

A further small increase in efficiency can be obtained for higher current densities by feeding the cathode with humidified air. In this way, the cathode can be fed with a higher air flow rate without cooling the cell to a lower temperature, where methanol oxidation would slow down significantly, thus reducing cell voltage and efficiency.

Acknowledgements

Open access funding enabled and organized by Projekt DEAL.

List of Symbols

$c_{P(Air)}$	Heat capacity of air / W g ⁻¹ K ⁻¹
CFR	Cathodic flow rate at the cell inlet / L cm ⁻² s ⁻¹
CFR _{Out}	Cathodic flow rate at the cell outlet / L cm ⁻² s ⁻¹
F	Faraday constant / 96,485 A s mol ⁻¹
ΔH_v	Enthalpy of evaporation of water / W mol ⁻¹
i	Current density / A cm ⁻²
i_p	Permeation current density / A cm ⁻²
n	Amount of methanol consumed / mol
Q_A	Heat used for heating air in the cell / W cm ⁻²
Q_F	Heat generated due to Faradaic loss / W cm ⁻²
Q_V	Heat generated due to voltage loss / W cm ⁻²
Q_W	Heat used for evaporating water / W cm ⁻²
p_{H_2O}	Water vapor partial pressure / Pa
R	Gas constant / 8.314 J mol ⁻¹ K ⁻¹
t	Time / s
T	Cell temperature / K
ΔT	Temperature difference / K
U_{Cell}	Cell voltage / V
U_G	Voltage corresponding to the Gibbs free enthalpy / V
U_{HHV}	Voltage corresponding to the higher heating value / V
U_{LHV}	Voltage corresponding to the lower heating value / V
V_{Cons}	Volume of oxygen consumed / L cm ⁻² s ⁻¹
V_{Gen}	Volume of CO ₂ generated / L cm ⁻² s ⁻¹
z	Number of electrons transferred / 6
η_{HHV}	Efficiency corresponding to the higher heating value
η_{LHV}	Efficiency corresponding to the lower heating value
η_G	Efficiency corresponding to the Gibbs free enthalpy
$\rho_{(Air)}$	Density of air / g L ⁻¹

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