45% Cell Efficiency in DMFCs via Process Engineering

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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, leading to higher over-potential, as well as to methanol permeation, which leads to a loss of fuel and mixed potential at the cathode. At the same time, permeation is helpful to keep the cell at a useful operating temperature of 70 °C in spite of the cooling effect of water evaporating at the cathode.

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 (Figure 1a).

In this paper, we show how these effects have to be balanced using air-flow rates calculated to ensure thermal equilibrium. As a result, it is possible to achieve electrical cell efficiencies of up to 44% of the lower heating value of methanol in a self-heating DMFC (Figure 1b). Another small increase in efficiency can be achieved by using humidified air at the cathode. This allows the use of a higher cathode volume flow while still maintaining a high cell temperature.

Figure 1. a) Change in performance at constant current density with a change in methanol feed (left); efficiency and power density of all autothermal operating states (right, line through maxima is a guide for the eye).
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 due 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 an assumed system efficiency of 80%, a cell efficiency of 43.75%.

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. In the literature, a number of publications determining 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. Efficiencies of up to 25% were achieved, however.\(^4\) Casalegno et al. studied how these parameters influence methanol permeation and obtained similar results with efficiencies of up to 24%.\(^5\) 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.\(^6\) A similar efficiency was experimentally obtained by Park et al. in a self-heating DMFC stack.\(^7\) Yeh et al. compared efficiency data from a 3-cell stack, fed with heated methanol and a self-heating, 26-cell stack.\(^8\) They found that the efficiency of the heated stack reaches up to 35% (not considering the energy needed to heat up the methanol), while the self-heating stack achieved only 25% efficiency. The main difference in operating parameters was in the cathode air flow rate, which was reduced from 28 ml/cm\(^2\)min to 8 ml/cm\(^2\)min 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 4000 operating hours. During this time, the efficiency degraded to 25% in the heated 3-cell stack and to 16% in the self-heating, 26-cell stack. Gao et al. estimate cell efficiency from a model they do not describe in detail to be 35%\(^9\) while assuming the system’s efficiency to be 82%. In their review of DMFCs,\(^10\) Joghee et al. also mention that efficiencies of up to 35% have been experimentally demonstrated in single cells. They assume that efficiencies up to 40% 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.

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. 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.

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. 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*42 mm. 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/cm².

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.

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 ip using Faraday’s law (1):

\[ n = (i + ip) \frac{t}{zF} \]  

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/cm² of active cell area, n is obtained in mole per cm² and minute if t is chosen as 60 s.
Thus, for a current density of 0.1 A/cm² and permeation current density of 0.01 A/cm², 0.0114 mmole 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.

| c (inlet) | Methanol flow rate | Methanol feed rate | Current density | Methanol permeation | Methanol consumption | c (outlet) |
| mole/l | ml/cm²min | mmole/cm²min | A/cm² | A/cm² | mmole/cm²min | mole/l |
|---|---|---|---|---|---|---|
| 1 | 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 | 0.6 | 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 |

### 3. Results

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 0.5 M to 1 M methanol and flow rates between 0.055 ml/cm²min, the cell voltage at low current densities was highest for low concentrations and low flow-rates (Figure 2). 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. This can be used as an alternative for reducing the concentration. At a current density of 0.3 A/cm² methanol permeation for 1 M of 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 M methanol and a flow rate of 0.055 ml/cm²min, 0.055 mmole/cm²min are fed into the cell, while at 0.75 M methanol and 0.44 ml/cm²min, 0.33 mmole/cm²min are fed into the cell. Of this amount, 0.032 mmol/cm²min are consumed, so
in the first case 58% of the methanol is consumed and the methanol concentration at the outlet is reduced to 0.42 M. In the second case, less than 10% are consumed and the methanol concentration at the outlet is 0.68 M (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/cm², cell voltage significantly decreases. Apparently, under these conditions the methanol concentration at the outlet is too low for higher current densities.

It is, therefore, 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 2. To facilitate interpretation of the results, points obtained at the same current density are connected to lines of a certain color.

![Image](image_url)

**Figure 3. Efficiency over power density for concentrations and flow rates as in Figure 2. Data obtained at the same current density are connected by lines (left); change in performance at 0.2 A/cm² with change in the methanol feed (right).**

The general shape of these curves is shown in Figure 3 for a current density of 0.2 A/cm². 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/cm², 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.

On the left side of Figure 4, 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.
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.

![Figure 4. Efficiency over power density as in Figure 2. Data obtained at the same methanol concentration and flow rate are connected by lines (left); efficiency over the current density for different flow rates of 0.3 M methanol (right).](image)

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 4, 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 on the left in Figure 5.

![Figure 5. Efficiency over current density for low concentrations and 0.22 ml/cm²min flow rate (left); and for low concentrations and low flow rates (right).](image)

It remains to be determined whether reducing the flow rate or reducing the methanol concentration is the better way to increase DMFC efficiency. This is shown in Figure 5 (right). 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 ml/cm²min and 0.015 ml/cm²min, respectively, while in the other case the flow rate was kept at 0.22 ml/cm²min and the methanol concentration was decreased to 0.25 M and 0.2 M. 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 (0.2 M methanol at 0.22 ml/cm²min) 0.044 mmol/cm²min of methanol were fed into the cell, whereas for the lowest flow rate (0.015 ml/cm²min of 0.5 M methanol), only 0.0075 mmol/cm²min were provided; less than 20%. As shown in Table 1, this leads to an outlet concentration of 0.13 M or 0.17 M, respectively. As a consequence, the methanol concentration is more homogenously 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 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 5 (right).

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.

![Figure 6. Highest efficiency for each combination of the methanol concentration and flow rate for dry and humidified air.](image)

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 6, 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 6 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/cm².

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/cm² and 37.5% efficiency was reached at more than 50 mW/cm². 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.

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.

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