Process analysis of a liquid-feed direct methanol fuel cell system

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Abstract

Recently, a greatly increasing interest in solid polymer electrolyte fuel cells (PEFC) for a range of applications has been observed. The direct methanol fuel cell (DMFC) based on a PEFC uses methanol directly for electric power generation and promises technical advantages, for example, for power trains.

This study analyses the interaction between a DMFC stack fed with a liquid aqueous methanol solution and the peripheral system equipment. A simulation model of a DMFC system for mobile applications (from methanol to net electricity) is presented to calculate system efficiencies on the basis of thermodynamic engineering calculations.

Based on the simulation calculations, useful operating requirements can be specified. To optimise the performance of DMFC systems, it is necessary to consider the operational characteristics of all the components required in the system. There are worldwide activities to improve the performance of a DMFC stack, which depends on numerous operating parameters. But it is not sufficient to optimise only the current/potential curves of the fuel cell without taking all the consequences for the system into consideration. The results of the computer simulation presented here emphasise the difficulties in improving fuel cell performance without decreasing system efficiency and describes the consequences for the system's operation conditions.

Priorities are additionally set concerning the heat management of the fuel cell stack. In the case of liquid fuel supply, the water crossover through the membrane and the ensuing vapourisation at the cathode side impairs the thermal balance. Key operating parameters, which influence these effects, are pressure, temperature, air flow and methanol permeation rate. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the last few years, much progress has been made in the development of fuel cell systems for vehicular applications. The system of choice is the polymer electrolyte fuel cell (PEFC). This kind of fuel cell delivers high power densities at low temperatures and allows rapid response to changes in the power demand. In principle, there are two different ways for using the PEFC for traction power: hydrogen storage on-board or on-board generation of hydrogen by partial oxidation or heated steam reforming of liquid fuels like methanol or gasoline.

In addition to these solutions, the possibility of a direct electrochemical conversion of methanol in a direct methanol fuel cell (DMFC) is a new and very attractive alternative method, because no complex fuel processing is necessary and gas treatment is also redundant. The quite complex system of an indirect methanol fuel cell (IMFC) can be simplified. Moreover, a DMFC system promises higher system efficiencies, because there is no energy consumption for fuel reforming. In consequence, a significantly lower system size and lower costs at comparable power densities can be predicted [1,2].

In principle, two different concepts exist to utilise methanol directly. The fuel can be delivered to the fuel cell in a gaseous or liquid form. Vapour-feed cells operate at higher temperatures with enhanced performance. Nevertheless, most of the published examinations concentrate on the liquid-feed DMFC because no fuel vapouriser is neces-

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sary, it is possible to dispense a complex humidification of the membrane.

The anode is directly served by a liquid methanol/water mixture. The protons produced at the anode migrate through the electrolyte membrane to the cathode. The electrons travel through the external closed circuit.
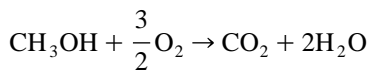
Anode reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-.$$
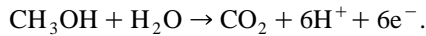
On the cathode the protons and the electrons react with the air oxygen to water.

Cathode reaction:

$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O.$$
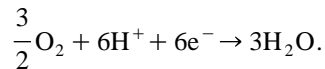
This leads to the overall cell reaction:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

(for liquid educts and vapour products: $E = 1.18$ V, $\Delta^R G = -685.3$ kJ/mol).

Some details of the mechanism of the reaction depending on the selected catalysts are not yet clear. Consequently, possible by-products, except for carbon monoxide, are not considered in the following study.

At present, the performance of a DMFC is, of course, clearly lower than that of a conventional hydrogen-feed PEFC. In the meantime, all over the world research programmes are concentrating on the development of higher DMFC performance. The main problem is that the electrochemical reaction of methanol is limited. In addition, methanol permeates through the membrane and oxidises at the cathode. This results in a mixed potential at the cathode. Additionally, part of the fuel cannot be used for power generation and the efficiency of the system decreases.

The results of the fuel cell performance are mainly influenced by the operating temperature and pressure. Increasing temperature and oxygen pressure leads to higher cell voltages. This has been illustrated, for example, by JPL [3], LANL [4,5] and the University of Newcastle [6]. But the methanol crossover is, on the other hand, controlled by cell temperature. Higher temperatures increase methanol crossover [7].

However, the development is still in the early stages and significant progress in performance can be expected. But there is not only the requirement for stack development. The process engineering analysis shows that the integration of the fuel cell in the system raises new problems. Optimising a complete fuel cell system makes it necessary to analyse the way in which the components interact. This study will present the results of simulation calculations of a liquid-feed DMFC system. The main objective will be the interaction between fuel cell stack and system components and the thermal balance of the stack depending on operating conditions.

2. Simulation of the fuel cell system

For the process engineering analysis, a commercial simulation program is used, which solves the equations of
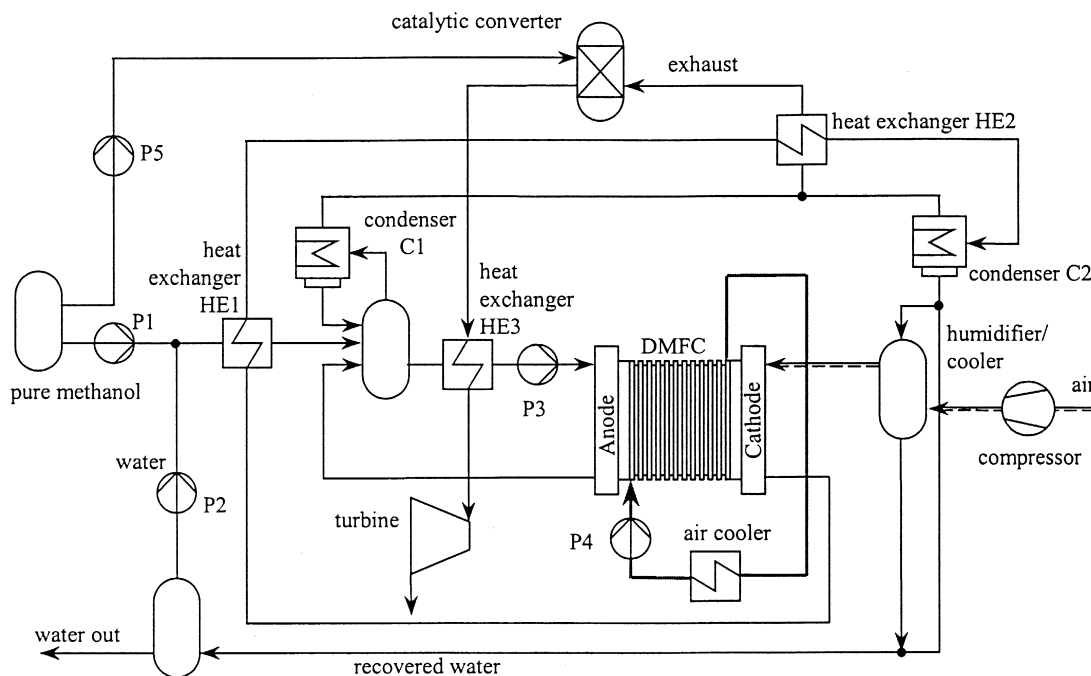

Fig. 1. Flowsheet of a liquid-feed DMFC system.

energy and mass balances. This program is only suitable for stationary investigations. Case studies identify favourable operating conditions. Input data defines the conditions required to solve the balances.

The program contains a number of components, such as heat exchangers, compressors, pumps and chemical reactors. These components can be used to build up a flowsheet describing the fuel cell system. For the fuel cell itself, it is necessary to develop a special discrete model, which is able to describe the processes taking place in the fuel cell depending on the current/potential characteristics. Fuel utilisation and the permeating rate of water and methanol through the electrolyte membrane can be varied.

For modelling a process, the use of appropriate thermodynamic methods and precise data is essential to obtain good results. The simulation program contains numerous proven thermodynamic methods for the calculation of thermophysical properties like the distribution of components between phases in equilibrium, liquid and vapour phase enthalpies, entropies and densities. A modified Soave–Redlich–Kwong equation (SRKM) has been chosen for the calculations [8]. This modification is based on the mixing rule of Panagiotopoulos–Reid and provides better predictions of properties for multicomponent systems. In addition to K-values, the SRKM equation may be used to predict the enthalpies and entropies for the liquid and vapour phases and for the densities of the vapour phases. The API method is selected for the predicted liquid phase densities [9].

In this paper, we discuss simulation results for a reference system design. Fig. 1 shows the flowsheet of this fuel cell system. The design is based on various experimental test-benches and on the requirements of the thermal balance and water balance of the system and is not optimised. In order to consider general effects, it is not necessary to use a "perfect" system in this study.

Water and methanol are pressurised to operating pressure and mixed. After preheating in the heat exchanger, HE1, the fuel will reach a circulation tank. In the heat exchanger, HE3, the dilute methanol reaches operating temperature. The pump, P3, finally compensates pressure losses and then the fuel reaches the stack. Unconverted methanol, the reaction products and excess water leave the stack and are rejected to the circulation tank, which also functions as a gas–liquid separator. The outgoing gas phase is cooled in the condenser, C1, and condensed water and methanol are recycled.

Compressed cathode air is humidified and cooled. In the fuel cell stack, the air takes up the produced and permeated water and leaves the stack at stack temperature. The thermal energy of the cathode exhaust gas is used in the heat exchanger, HE1, for fuel preheating. The remaining heat is used in the heat exchanger, HE2. In the condenser, C2, the exhaust is cooled and the condensed water is separated. Recovered water is used to humidify the compressed air. The residue is recycled to the fuel

circulation so that it is self-sufficient in water. The exhaust gas of the anode and cathode side is mixed, preheated in the heat exchanger, HE2, and possible methanol residues or other by-products are finally converted in the catalytic converter. Ultimately, the remaining pressure energy is used in a turbine. The cooling system in this example is a conventional water circuit combined with an air cooler. A fan is not considered in the energy balance. All the heat exchangers are constructed as countercurrent heat exchangers with a pinch point of 5 K at least.

For the present analysis, the following fixed operating conditions are taken as the point of departure.

Liquid feed.

1 molar aqueous methanol.

A constant water drag coefficient of 4 H_2O/H^+ is assumed in the range of temperature considered. The dependence of the water flux across a Nafion 117 membrane in contact with liquid water on the temperature is shown in Ref. [11]. In the case of 1 M methanol and dry oxygen, the water drag coefficient increases with temperature, from 2.85 H_2O/H^+ at 60°C, 3.4 H_2O/H^+ at 80°C to 5.1 H_2O/H^+ at 130°C. According to these results, an average drag coefficient is taken. In any case, the permeating rate of water has no significant influence on system efficiency.

If there are given absolute values for the stack heat duty or power generation in kW, these results are based on a methanol feed rate of 1 kmol/h (without the methanol for the catalytic burner).

The catalytic converter needs additional fuel to reach his operating temperature T_C. Menzer et al. [2] have shown that the operating temperature of the catalytic converter controls the system efficiency and that higher operating temperatures of the catalytic converter lead to decreasing system efficiency. Further development has to concentrate on reducing the temperature required for the catalytic burner. In this study, the catalytic converter works at temperatures between 125°C and 175°C. This assumption is an optimistic, theoretical assumption. Additionally, the results of the present study will only emphasise the influence of different operating conditions on the system efficiency and the stack heat duty under comparable constraints and the operating temperature of the catalytic converter has no influence on the heat balance of the stack.

Table 1
Fixed system design parameters

| Design parameter	Value
Fuel utilisation in DMFC	80%
Pump efficiencies	80%
Adiabatic compressor efficiency	60%
Adiabatic expander efficiency	50%
Pressure loss in the heat exchanger	20 mbar
Pressure loss in the fuel cell	50 mbar

Other defined parameters are summarised in Table 1.

The systems are characterised by the net system efficiency. In Eq. (1), the net system efficiency is defined as the ratio of the net power and fuel input according to the lower heating value of methanol ($LHV_{methanol}$ = 638.5 kJ/mol) (Eq. (1)). In the electrical net power, the power requirements of the subsystem auxiliaries have to be considered. Heat losses are completely disregarded in the investigations.

$$\eta_{system} = \frac{P_{net}}{\dot{n}_{methanol} LHV_{methanol}} . \qquad (1)$$

The main objective of the process engineering analysis is the influence of the following parameters on the system efficiency and the heat balance of the stack:

· temperature;
· pressure: The air or oxygen pressure is important for the cell voltages. In most investigations there are no differences between the anode and cathode pressure, unless explicitly staked;
· air-to-fuel ratio: The air-to-fuel ratio λ is defined as the ratio between the supplied oxygen and the stoichiometric oxygen demand relative to methanol utilised:

$$CH_3OH + \frac{3}{2}\lambda O_2 \rightarrow CO_2 + 2H_2O + \frac{3}{2}(\lambda - 1)O_2 ;$$
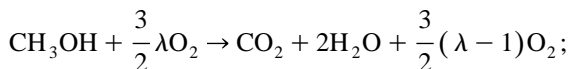
· cell voltage;
· methanol permeation rate.

3. Results

The proposed system simulation is able to calculate system efficiencies and the thermal balance of the fuel cell stack and leads under different operating conditions to the following results.

3.1. General aspects

3.1.1. Electrical system efficiency

The results presented in Fig. 2 are based on published U-i characteristics [3,4]. The single cell data is transferred to the stack performance.

In both cases, the chosen electrolyte is Nafion 117 and the methanol concentration is 1 molar. The systems only differ in pressure and temperature. In the system calculations, the assumed value for the air-to-fuel ratio is 1.75 and the catalytic converter works at 175°C. The results do not consider the possibility of methanol permeation through the electrolyte.

The comparison of the two system efficiencies shows a good example of the gap between the efforts to optimise cell performance and obtain good system efficiency. The power densities have nearly the same quality. Nevertheless, there is a significant difference between the calculated system efficiencies. The average efficiency difference amounts to about 2% points. For example, at a cell voltage of 400 mV, a stack temperature of 90°C and a pressure of 2.4 bar [3], a system efficiency of 28.5% is reached. At a
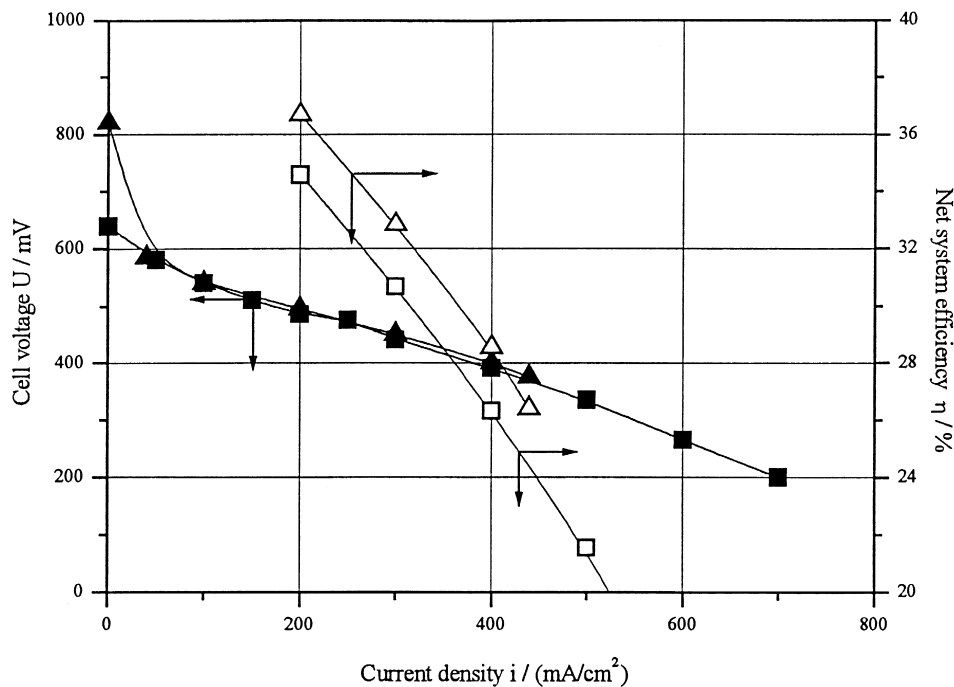

Fig. 2. System efficiencies for different operating conditions and comparable U-i characteristics (no methanol permeation). Legend 2 — Net system efficiencies: $-\square-$, T = 110°C, p_A = 1.84 bar, p_K = 3 bar, 1 M methanol, air; λ = 1.75, T_C = 175°C; $-\triangle-$, T = 90°C, p = 2.4 bar, 1 M methanol, air, λ = 1.75, T_C = 175°C. Current/potential curves: $-\blacksquare-$, Nafion 117, T = 110°C, p_A = 1.84 bar, p_K = 3 bar, 1 M methanol, air [4]; $-\blacktriangle-$, Nafion 117, T = 90°C, p = 2.4 bar, 1 M methanol, air [3].
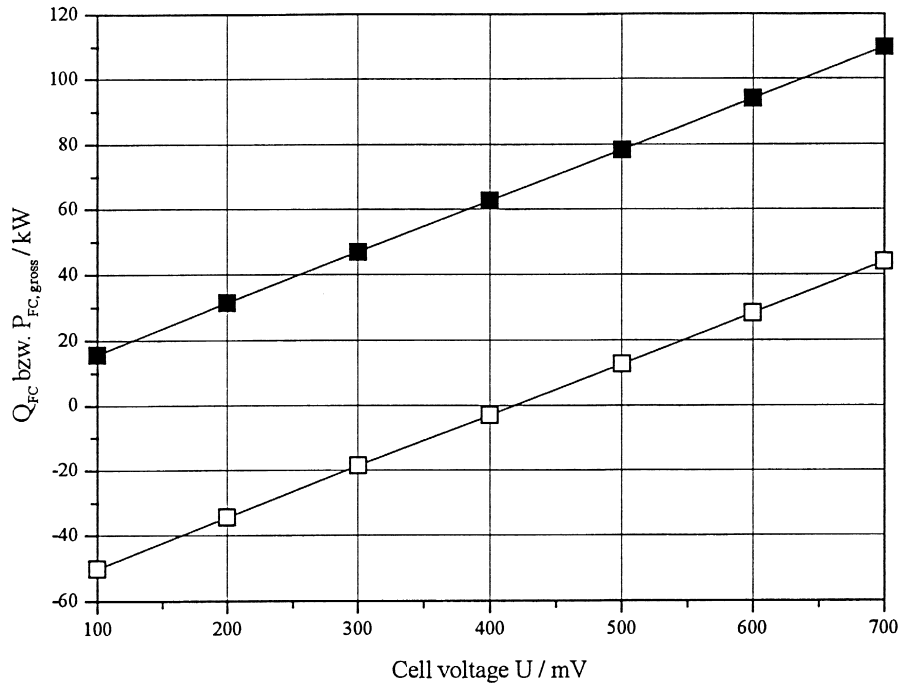
Fig. 3. Dependence of the cell voltage on the heat duty and the electrical power of a DMFC stack (no methanol permeation, $T = 85°C$, $p_{FC} = 1.5$ bar, 1 M methanol, air, $\lambda = 2.5$, $H_2O_{perm} = 4\ H^+$). Legend 3: $-\square-$, Heat duty Q_{FC}; $-\blacksquare-$, Gross electric power $P_{FC,gross}$.

temperature of 110°C and a pressure on the anode side of 1.84 bar and on the cathode side of 3 bars [4], the system efficiency achieves only 26.3%. Increasing the air-to-fuel ratio leads even to differences.

More attention should be paid to this phenomenon in fuel cell development. To evaluate a U-i characteristic, the operating conditions have to be considered because they have a great influence on the energy output of the system.
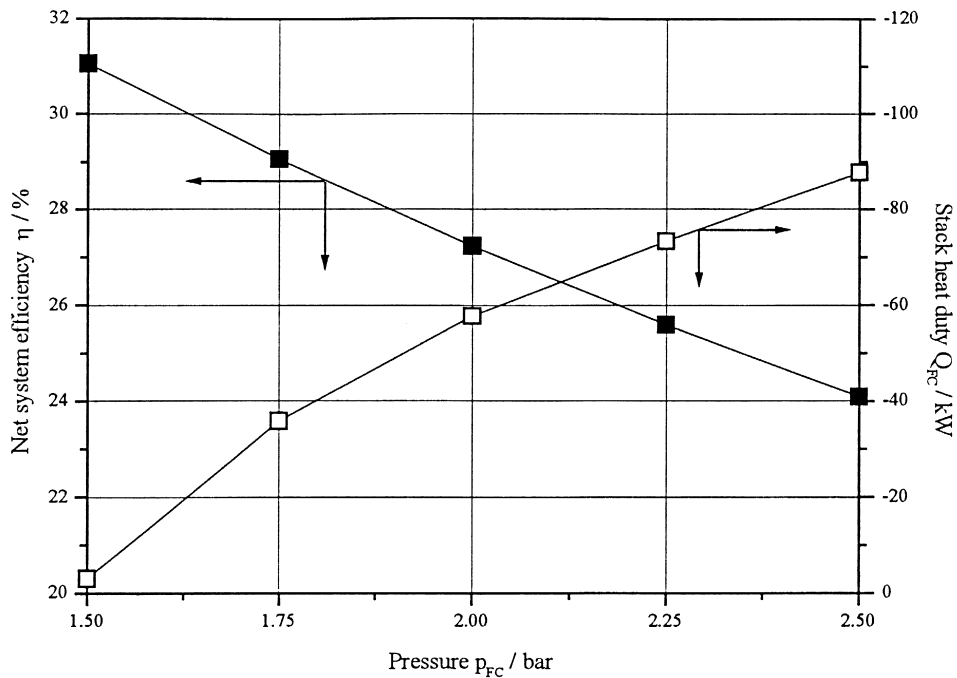

Fig. 4. Effect of the operating pressure on the system efficiency and the heat duty (no methanol permeation, $T = 85°C$, $U = 400$ mV, 1 M methanol, air, $\lambda = 2.5$, $T_C = 125°C$, $H_2O_{perm} = 4\ H^+$). Legend 4: $-\blacksquare-$, net system efficiency η; $-\square-$, stack heat duty Q_{FC}.

Process engineering analysis is an effective tool to investigate these interactions.

3.1.2. Thermal balance of the DMFC stack

The thermal balance of the stack is an important aspect for stable system operation and, therefore, a main objective of these simulation calculations. A large part of the fuel energy is converted into heat inside the stack. The heat flow, which is produced in combination with a specific electric cell voltage, decreases with increasing cell voltage.

Fig. 3 provides an insight into the energy balance of the stack. Waste heat from the fuel cell stack is, by definition, negative. The electrical power generation of the stack is increases depending on the cell voltage. The heat duty decreases accordingly.

Fig. 3 shows that for the assumed operating parameters ($T = 85°C$, $p = 1.5$ bar, $\lambda = 2.5$) at a cell voltage of approximately 420 mV, no heat duty results. Increasing the cell voltage leads to a lack of heat because the permeating water vapourises at the cathode side. Either the stack has to be heated to supply the evapouration enthalpy or the operating temperature decreases. These two alternatives are not useful solutions.

One well-known advantage of liquid-feed DMFC systems in comparison to vapour-feed systems is the possibility of stack cooling with the reactants [11]. The results of this study indicate areas of operating conditions, which can minimise the expenditure of cooling for choosing optimised parameters. Additionally, in these investigations, we discuss the potential demand of stack heating for liquid–feed systems. Of course, the temperature and humidification of the supplied air have a decisive influence on the stack heat duty. To prevent a negative thermal balance of the stack, the solution is to provide water-vapour saturated air at or above cell temperature. But this condition cannot be fulfilled by the heat management of the fuel cell system without additional energy expenditure, which leads to decreasing system efficiency.

3.2. Parameter variation

In addition to the cell voltage the temperature, the pressure, the air-to-fuel ratio and the methanol permeation rate influence the excess heat of the stack. The following calculations are always based on a cell voltage of 400 mV and the influence of the varied parameters on the cell performance is not considered. The results show, as an example, their influence on the system efficiency and the excess heat.

3.2.1. Pressure

The influence of the pressure on the system efficiency is very noticeable. Fig. 4 shows the dependence of the system efficiency on the pressure for constant operating conditions ($T = 85°C$, $\lambda = 2.5$).

In these investigations, the anode pressure corresponds to the cathode pressure. The energy output decreases nearly linearly. The second curve shows the resulting excess heat. Pressures under 1.5 bar mean that no waste heat arises.
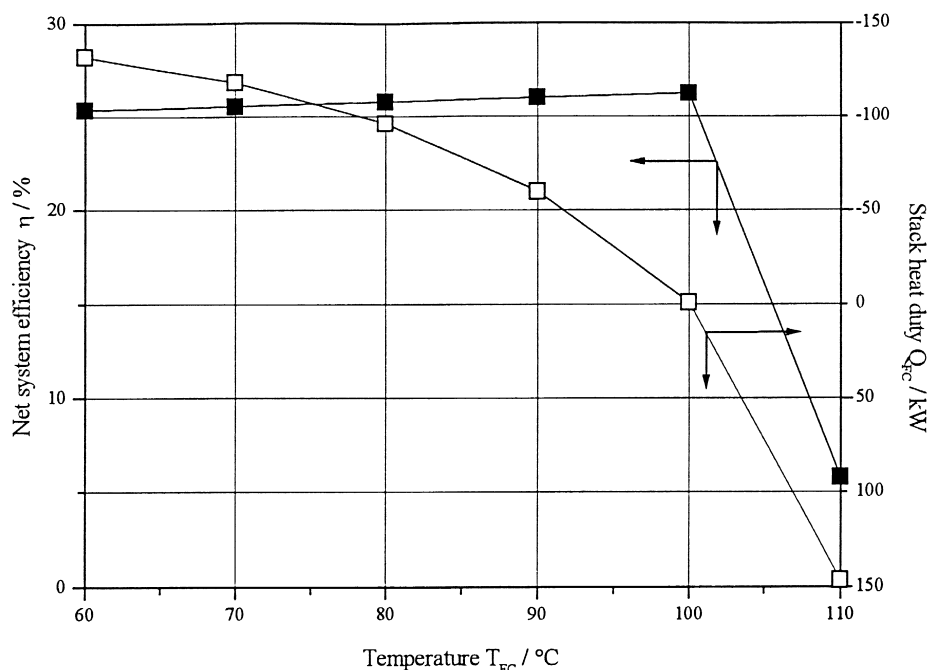
Fig. 5. Influence of the stack temperature on the system efficiency and the heat duty (no methanol permeation, $p_{FC} = 2.4$ bar, $U = 400$ mV, 1 M methanol, air, $\lambda = 2.5$, $T_C = 150°C$, $H_2O_{perm} = 4$ H^+). Legend 5: $-\blacksquare-$, net system efficiency η; $-\square-$, stack heat duty Q_{FC}.
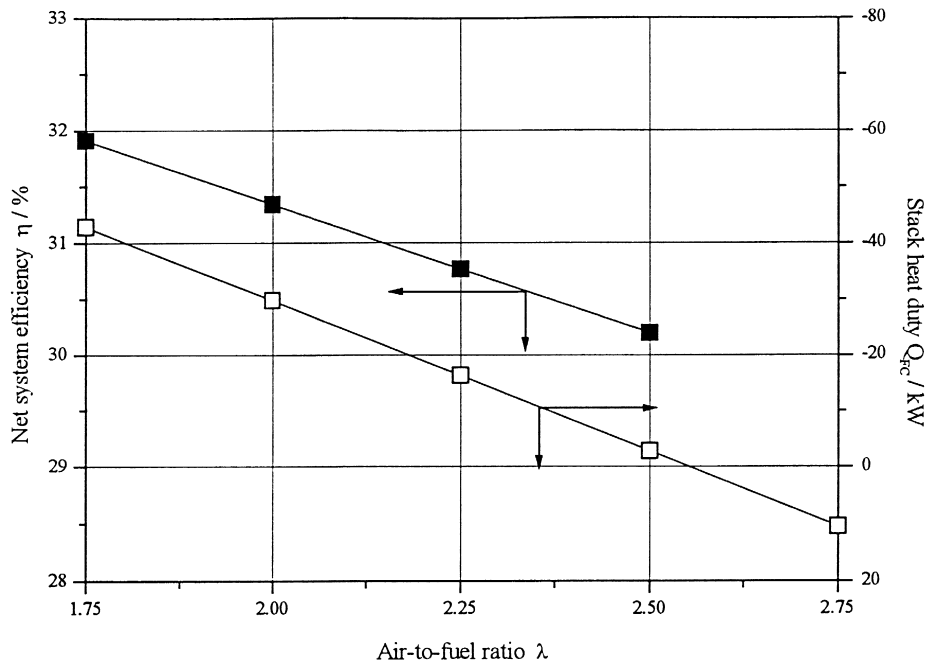
Fig. 6. Influence of the air-to-fuel ratio on the system efficiency and the heat duty (no methanol permeation, $T_{FC} = 85°C$, $p_{FC} = 1.5$ bar, $U = 400$ mV, 1 M methanol, air, $T_C = 150°C$, $H_2O_{perm} = 4$ H^+). Legend 6: $-\blacksquare-$, net system efficiency η; $-\square-$, stack heat duty Q_{FC}.

3.2.2. Temperature

The effect of the stack temperature on the electrical system energy output and the heat duty can be seen in Fig. 5.

Varying the temperature between 60°C and 90°C has only a marginal influence on the system efficiency, although the dependence of the excess heat on the temperature is more intense. At a stack temperature of 100°C, the

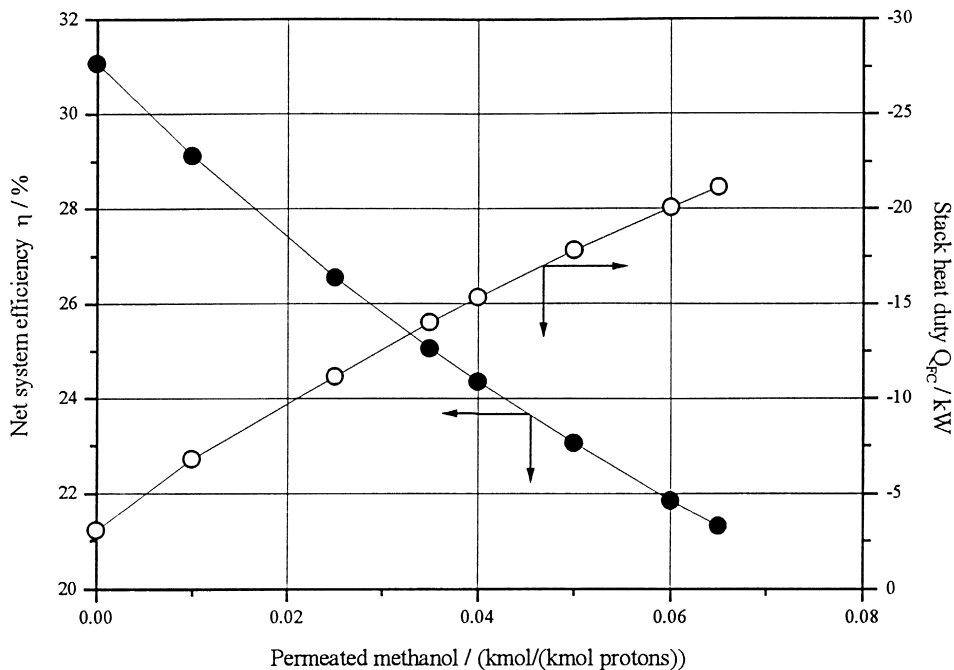
Fig. 7. Influence of the methanol permeation on the system efficiency and the heat duty ($T_{FC} = 85°C$, $p_{FC} = 1.5$ bar, $U = 400$ mV, 1 M methanol, air, $\lambda = 2.5$, $T_C = 125°C$, $H_2O_{perm} = 4$ H^+). Legend 7: $-\blacksquare-$, net system efficiency η; $-\square-$, stack heat duty Q_{FC}.
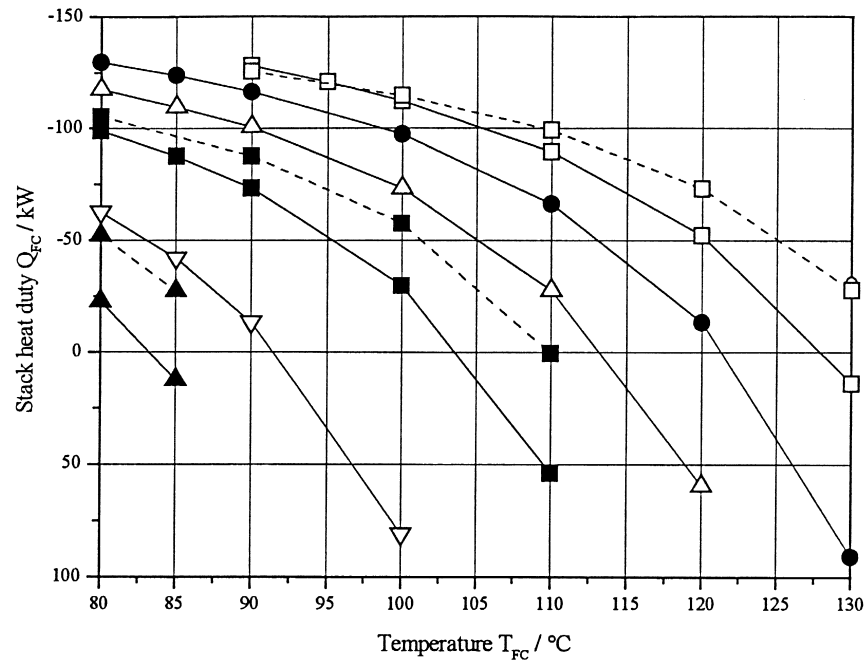
Fig. 8. Favourable fuel cell operating conditions for the introduced DMFC-System (no methanol permeation, $U = 500$ mV, 1 M methanol, air, $H_2O_{perm} = 4$ H$^+$). Legend 8 — Operating pressure: $-\blacktriangle-$, 1.5 bar; $-\triangledown-$, 2 bar; $-\blacksquare-$, 3 bar; $-\triangle-$, 4 bar; $-\bullet-$, 5 bar; $-\square-$, 6 bar; $-\bigcirc-$, 7 bar. Air-to-fuel ratio: $-\blacktriangle-$, $\lambda = 2.5$; $--\blacktriangle--$, $\lambda = 1.75$.

excess heat is about zero. In this example, the system efficiency has been calculated for the case of heating the stack. Because of the additional methanol needed for the heating, the system efficiency decreases rapidly by about 20% points. This indicates that heating the stack is not energetically meaningful.
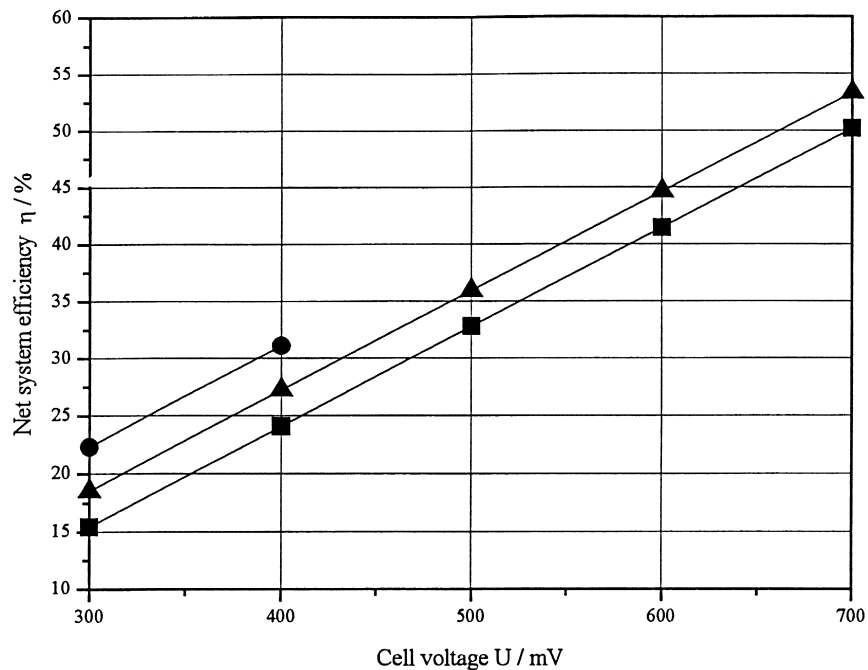

Fig. 9. Influence of the pressure on the system efficiency depending on the cell voltage (no methanol permeation, $T_{FC} = 85°C$, 1 M methanol, air, $\lambda = 2.5$, $T_C = 125°C$, $H_2O_{perm} = 4$ H$^+$). Legend 9 — Operating pressure: $-\bullet-$, 1.5 bar; $-\blacktriangle-$, 2 bar; $-\blacksquare-$, 2.5 bar.

3.2.3. Air-to-fuel ratio

The system shows a marked increase in efficiency when the air-to-fuel ratio is reduced (Fig. 6). In comparison, the influence of the air-to-fuel ratio on the excess heat is shown in the same figure. Less air leads to higher amounts of heat duty. In the example considered ($T = 85°C$, $p = 1.5$ bar, 1 M methanol, $U = 400$ mV), there is no excess heat at $\lambda = 2.55$.

3.2.4. Methanol permeation

Finally, the methanol permeation should be considered. Fig. 7 shows the results when the amount of permeating methanol is varied. The influence of the system efficiency is dramatic. Assuming that the permeating methanol oxidises completely at the cathode, the excess heat increases with higher permeation rates.

4. Discussion

With the proposed system and the parameters considered above (cell voltage, pressure, temperature, air-to-fuel ratio and methanol permeation), it is possible to calculate useful areas for operating a liquid-feed DMFC system.

The criterion is the excess heat of the stack because it has been shown that stack heating is not useful. Fig. 8 shows the results for a constant cell voltage of 500 mV. The isobars from 1.5 to 7 bar run as a function of temperature. In some cases, a smaller air-to-fuel ratio of 1.75 has also been considered.

An operating temperature of 110°C, for example, requires a minimum pressure of 3 bars and an air-to-fuel ratio of 1.75. Higher values for λ make higher pressures necessary. Increasing the cell voltage to more than 500 mV also leads to unstable conditions in the stack heat balance. Temperatures greater than 110°C are generally not useful for the liquid-feed DMFC system because of the resulting high compression requirements.

In the preceding investigations, the influence of the varied parameters on the cell voltage has been disregarded. Only the pure influence of the parameter on the system has been considered.

It is, for example, well-known that increasing the pressure on the cathode side leads to higher cell voltages. But this parameter also involves lower system efficiency. The optimum between the electrical requirements of the compressor and the power density of the DMFC stack can be identified in a detailed process engineering analysis. For the liquid-feed DMFC system considered with a stack temperature of 85°C and $\lambda = 2.5$, the results for different operating pressures are represented in Fig. 9.

Raising the pressure from 1.5 to 2 bar makes a higher cell voltage of about 45 mV necessary to reach the same electrical efficiency. The pressure can be further increased from 2 to 2.5 bar by parallel raising of the cell voltage. About 35 mV can balance the additional electrical losses. The straight line for the pressure of 1.5 bar ends at 400 mV because of problems regarding the thermal balance of the stack.

5. Conclusion

The examples presented show the importance of a detailed analysis of the mass end energy flows in fuel cell systems. High power densities of a fuel cell do not guarantee high system efficiencies. The results clearly indicate areas of operating conditions where a liquid-feed DMFC is not useful regarding the thermal balance of the stack. On the other hand, the liquid-feed fuel cell makes it possible to minimise the expenditure of cooling by choosing optimised parameters.

Further developments for improving the U-i characteristics of DMFCs should always take into account the interactions between fuel cell and system. Stack engineering has not yet been optimised and further development work on catalysts and the electrolyte is necessary. But improvements in performance are very likely. In addition, industrial suppliers will have to work on compressors, expanders and other components to improve the system efficiency.

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