

Performance and methanol permeation of direct methanol fuel cells: dependence on operating conditions and on electrode structure

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Abstract

Investigations are presented to determine the dependence of the performance of direct methanol fuel cells (DMFCs) and the methanol cross-over rate on the operating conditions, on the structure of the electrodes and on the noble-metal loading. It is shown that performance and methanol permeation depend strongly on cell temperature and cathode air flow. Also, methanol permeation can be reduced significantly by varying the anode structure, but the changed electrode structure also leads to somewhat lower power densities. The metal loading is varied at the anode and cathode affecting the cell performance. Furthermore, the differences between supported and unsupported catalysts are compared. We discuss the optimum conditions for the DMFC operation considering the various important factors. The discussion is focussed on finding a compromise between fuel cell performance, fuel utilization and metal loading.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising electrochemical energy converters for a variety of applications because of their system simplicity. The liquid-feed system does not require any fuel processing equipment and can be operated at even room temperatures. This concept may also be advantageous with respect to water management and stack cooling. Therefore, a high potential is foreseen in applications like transportation, in decentralized power generation and, most importantly, for portable devices [1,2]. The main problems associated with liquid-feed DMFCs are the low power density and low fuel utilization. This is related to the methanol and water permeation through the membrane and the slow electrode reaction kinetics. It is noted, however, that under certain conditions the high water permeation is also of advantage since no humidification of cathode gases is required. Due to the slow reaction kinetics, a high noble metal loading is necessary for acceptable performance [1,3–5].

The performance of the DMFCs can be improved by taking advantage of the pronounced thermal activation of

the electrochemical reactions: For instance, Arico et al. have reported high performances of DMFC single cells at 130 °C [6]. However, the increase in temperature is limited in liquid-feed systems since high temperature requires the build-up of high pressures in the anode compartment which would also require high pressures at the cathode side leading to dramatically reduced system efficiencies [7]. Furthermore, high temperature causes a dramatic increase in methanol cross-over rates leading to low fuel utilization and lower cell voltage. Thus, high catalyst loadings are often required to enhance the performance of the anode and cathode resulting in increased costs. Even though Nafion® and its variants are the most commonly used membranes against which other membranes are compared, these membranes exhibit insufficient properties for the direct methanol application. In particular, membrane properties need to be improved with respect to water balance and methanol crossover which can lead to a loss of 30% or more of the methanol fuel depending on the load [8–11]. Hence, there is a need to diminish the catalyst loading in the DMFC at the cathode and anode and to prevent methanol crossover as well as water crossover by either new materials or optimized operating conditions [12,13]. Recently, progress has been achieved in the development of new membrane materials with significantly reduced methanol permeation [3,14].

Another important consideration for improving performance of DMFCs is the electrode structure as well as the

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interface between the membrane and the electrode. The performance of DMFCs can be improved by varying the microstructures of membrane electrode assemblies (MEAs) in order to optimize the two phase transport at the anode (liquid feed, gaseous CO₂ removal) and cathode (gaseous feed and liquid water removal). Considering the complexity of the structures of the electrode and the gas diffusion layers (GDLs), it is not surprising that no consensus has been reached in the literature on the optimal structure and properties of the electrodes. A recent publication from Wei et al. states that a hydrophilic thin film at the anode is advantageous for the performance of DMFCs [15]. Nonetheless, Wei et al. found that in addition to the hydrophilic thin film an intermediate PTFE content of 20 wt.% exhibits maximum performance. On the other hand, Dohle et al. found no direct correlation of the power density with the PTFE content but a dependence on volume fraction of hydrophobic pores [8]. A recent publication by Nordlund et al. [16] reports a significant improvement when increasing the PTFE content in the anode catalyst layer. This improvement is attributed to a more effective mass transport in the active layer and the reported improvement is quite pronounced considering that the electronic conductivity of the electrode is notably reduced when increasing the PTFE content.

In this contribution, we address the main issues in the DMFC development and describe the strategies for optimizing DMFCs with regard to performance, energy efficiency and costs: Relationships between performance and operating conditions, between performance and electrode structure as well as between performance and precious metal loading are derived from numerous measurements. In addition to improving the power density, the reduction of methanol crossover is a major consideration in the development of DMFCs. Therefore, we discuss the measured methanol permeation rate as a function of operating conditions demonstrating that these conditions have to be chosen carefully to maintain a high Faradaic efficiency $\eta_{\text{far}} = I_{\text{cell}} / (I_{\text{cross-over}} + I_{\text{cell}})$.

2. Experimental

Membrane electrode assemblies were prepared similar to the procedure reported by Wilson and Gottesfeld [17]. The catalyst inks are prepared by dispersing unsupported or supported catalyst in suprapure Millipore water. Then Nafion[®] solution is added to obtain the wanted Nafion[®] content in the ink. Nafion[®] is necessary both for the binding of the electrode as well as for providing proton conductivity to the active layer. The alcoholic solution in the spraying procedure was considered a potential hazard due to the possibility of inflammation. Therefore, an alcohol-free Nafion[®] solution was prepared in a rotation evaporator using a 15 wt.% Nafion[®] solution with a corresponding equivalent weight of EW 1100. During evaporation, suprapure Millipore water

was added and therefore a diluted solution with a Nafion[®] content of 5–8% was obtained.

The preparation of the catalyst ink consisted in stirring it for at least 3 days. Only after this preparation procedure, electrodes layers with sufficient binding to the electrolyte could be produced. However, if the ink is stirred too extensively (>2 weeks) lower power densities especially at higher temperatures were observed. It is assumed that this is due to changes in the powder morphology which also can lead to blocking of the spraying nozzle.

The electrolyte membrane (Nafion[®] 105) is prepared in the usual way before being coated with catalyst [12]. The gas diffusion electrodes are prepared by a spraying directly onto the membrane: the wet membrane is fixed in a frame before being coated with catalysts. After fabricating the electrodes by spraying, a tempering step at 135 °C for >25 min in an oven follows. The catalyst loading is calculated by comparing the weight of the MEA after drying with the weight of the membrane and the catalyst content of the ink.

The MEA is introduced in a dry state into a home-made graphite cell with an active area of 25 cm² and a serpentine flow field with one channel of 1 mm × 1 mm. As gas diffusion layers teflonized or non-teflonized carbon papers are used (e.g. Toray TGP-120, 25% PTFE, compression by about 40% in the cell measured by $c = 1 - (l_{\text{end}}/l_{\text{start}})$ was found, where l_{start} and l_{end} are the thickness of the GDL at the before and after assembling of the cell, respectively).

The test station for the single cell DMFC measurements controls the important parameters for fuel cell application like cell temperature, humidification of gases, pressure in the anode and cathode chamber, mass flow, etc. The pressure is measured at the outlet of cathode and anode compartment. The aqueous methanol solution is used in a single flow through the cell without recirculation into a reservoir in order to maintain a constant methanol concentration. Temperatures of cell, humidifiers and other components are regulated by an eight-channel Watlow controller. The cell temperatures are established with the help of four heating cartridges which are introduced into aluminium endplates of the cell. Performance curves were obtained using an electronic load from ITS GmbH (model ITS 7141–2) at either constant currents or voltages. At the cathode exhaust a CO₂ sensor from Fisher-Rosemount with a detection limit of 1% of CO₂ in the cathode exhaust gas is used. In the measurement range, the specified error of the sensor is 2% of the full range. In our case, the methanol crossover is determined by monitoring the CO₂ flux in the cathode affluent gas using the optical IR CO₂ sensor. The method is based on the assumption that methanol permeating through the membrane is completely oxidized to CO₂. This can be achieved in a simple way by introducing an afterburner in front of the sensor. The catalytic afterburner (with Pt–Al₂O₃ catalyst) is operated at 160 °C and it was checked that all unconverted methanol at the cathode is reacted to CO₂. Dohle et al. [9] state that a large error is made with CO₂ sensors at the cathode due to the amount of carbon dioxide crossing over

from the anode to the cathode outlet due to diffusion. In that study, it is noted that the CO_2 diffusing through the membrane may even be higher than the amount of CO_2 formed at the cathode by methanol oxidation. As will be discussed in Section 3, this is not the case for the MEAs investigated here.

3. Results and discussion

3.1. Performance versus methanol cross-over

The performance of our DMFC operated with aqueous 1 M methanol solution is shown as a function of temperature in Fig. 1. Cell voltage versus current density as well as methanol permeation rate versus current density are displayed in Fig. 1A whereas Fig. 1B shows the dependence of power density on current density. A strong increase in power density with temperature is observed. At temperatures

above 100°C , power densities of more than 250 mW cm^{-2} at 0.5 V are obtained. However, these power densities are obtained with high noble-metal loadings in the range of approximately 11.7 mg cm^{-2} in the cell. The influence of the methanol fuel loss is also illustrated in Fig. 1, in which in addition to the cell voltage versus current density curves also the rate of methanol crossover is expressed in terms of equivalent current density and plotted on the right hand scale. The methanol flux to the cathode is often given by an equivalent current for the total oxidation to CO_2 in order to directly relate it to the cell current density. The methanol permeation rate diminishes with increasing current density since the conversion of methanol at the anode causes a decrease in the concentration gradient. At 600 mV for the measurement at $T = 110^\circ\text{C}$, the methanol lost due to permeation is in the range of 200 mA cm^{-2} and higher than the cell current density of 116 mA cm^{-2} . This means that the Faradaic efficiency $\eta_{\text{far}} = I_{\text{cell}} / (I_{\text{cross-over}} + I_{\text{cell}})$ corresponds to only 0.42 in

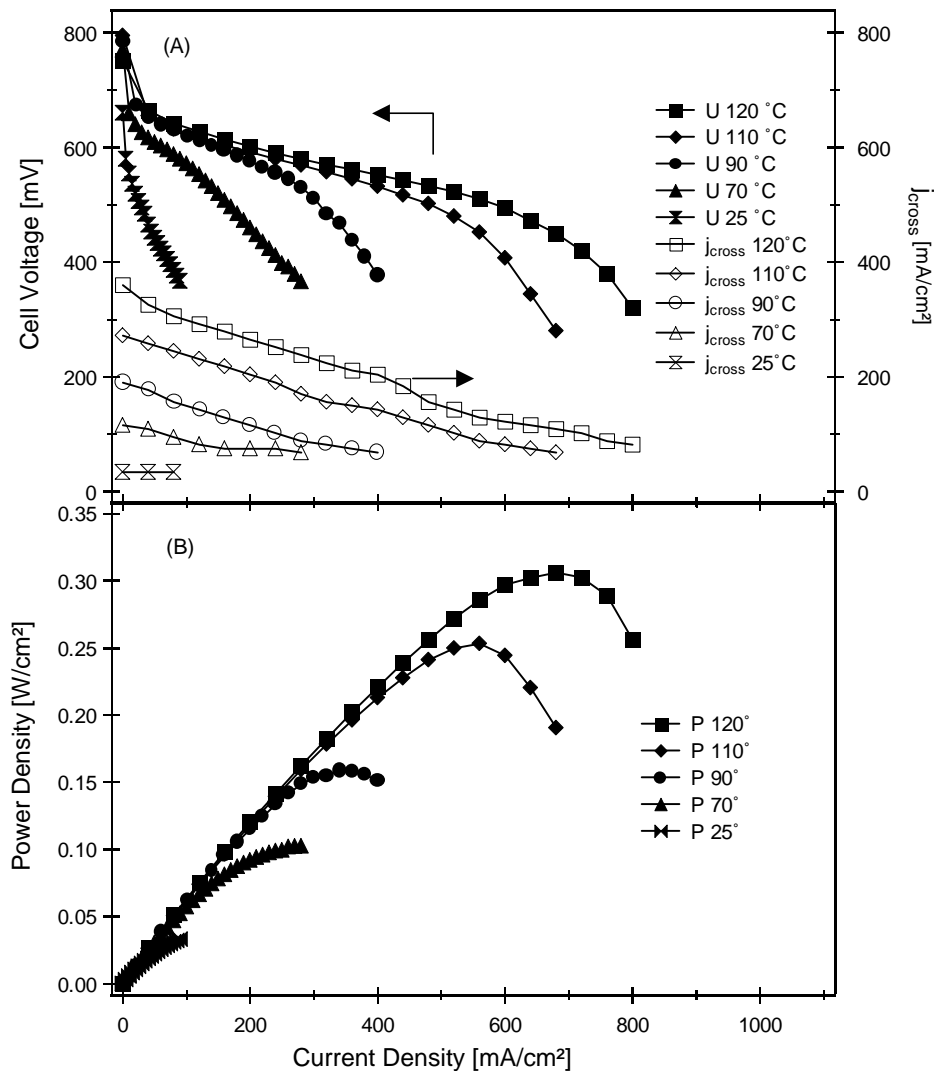


Fig. 1. DMFC performance curves for a MEA at different cell temperatures. (A) Cell voltage vs. current density (full symbols) and methanol permeation vs. current density (open symbols) measured with a CO_2 sensor. (B) Power density vs. current density. Cathode flow is 41 min^{-1} air, Nafion[®] 105, 1 mol l^{-1} methanol (4 ml min^{-1}). Anode: unsupported 5.4 mg cm^{-2} Pt–Ru, 2.5 bar pressure (outlet). Cathode: unsupported 6.3 mg cm^{-2} Pt, 4 bar pressure (outlet).

this case which would lead to cell/stack efficiencies well below 30%. At 0.5 V cell voltage, however, the equivalent methanol permeation current density is just 116 mA cm^{-2} and the cell current density is 480 mA cm^{-2} corresponding to a respectable Faradaic efficiency in the range of 0.8. The latter efficiency is acceptable and this rough estimation shows how careful the operating conditions of the DMFC have to be chosen with the presently used materials.

It is clearly seen in Fig. 1 that the methanol permeation increases with temperature and at higher temperatures the polymer backbone expands due to softening of the fluorinated chain leading to increased permeation of methanol as well as a higher water transport rate. The rate of methanol permeation with the present membranes restricts the concentration of methanol to values lower than 2 M solution and is consistent with reports in the literature [10,18].

It is also noted that at high current densities CO_2 generated from anode may permeate through the membrane thus reaching the cathode. The amount of CO_2 permeating to the cathode is responsible for an overestimation of methanol crossover. Dohle et al. [9] have pointed out that the amount of carbon dioxide passing from the anode to the cathode may even be higher than the amount of CO_2 formed at the cathode by methanol oxidation. Therefore, we have repeated the measurements with a new MEA under similar conditions reported above under normal DMFC operation and, secondly, using a hydrogen evolving cathode. The cathode is purged with hydrogen gas and in this case acts as a reference for characterizing mainly the anode process. The overpotential at the hydrogen cathode is thereby neglected. The measurements were carried out galvanostatically. Fig. 2 shows the comparison of cell voltage versus current density for normal

DMFC operation with air at 4 l min^{-1} and the overpotential of the anode versus current density for a MEA with similar noble metal loadings at 110°C and a hydrogen flow rate at the cathode of 0.3 l min^{-1} .

The MEA of Fig. 2 exhibits a somewhat lower power density but similar methanol permeation rate compared to the measurements at 110°C in Fig. 1. The overpotential of methanol oxidation for the same MEA is significant and values between 200 and 550 mV are observed depending on the current density. This is in agreement with the results reported by Dohle et al. [9] for the same cell temperature. The measurements with the hydrogen-evolving cathode were performed at a cathode flow rate of 0.3 l min^{-1} but no significant deviation of the overpotential was observed as a function of cathode hydrogen flow. Our observations are at variance with the results of Dohle et al. with regard to the importance of the CO_2 permeation from the anode to the cathode. Since the potential of the hydrogen cathode is in the range of -50 to -30 mV versus RHE, no oxidation of methanol can occur. Therefore, all detected CO_2 should correspond to the permeated carbon dioxide from the anode (in this case no afterburner is used). For our MEAs, the detected rates were below the sensitivity of the CO_2 sensor at a hydrogen flow rate of 4 l min^{-1} at the cathode. Therefore, a flow rate of 0.3 l min^{-1} was used which yields a low but detectable signal. The measurement is shown in Fig. 2 and the CO_2 permeation exhibits a weak dependence on current density. The variance may be attributed to the differences in electrode preparation and corresponding microstructure. In contrast to the MEA investigated here, Dohle et al. used carbon supported catalysts and different MEA preparation procedures which may result in different microstructures and

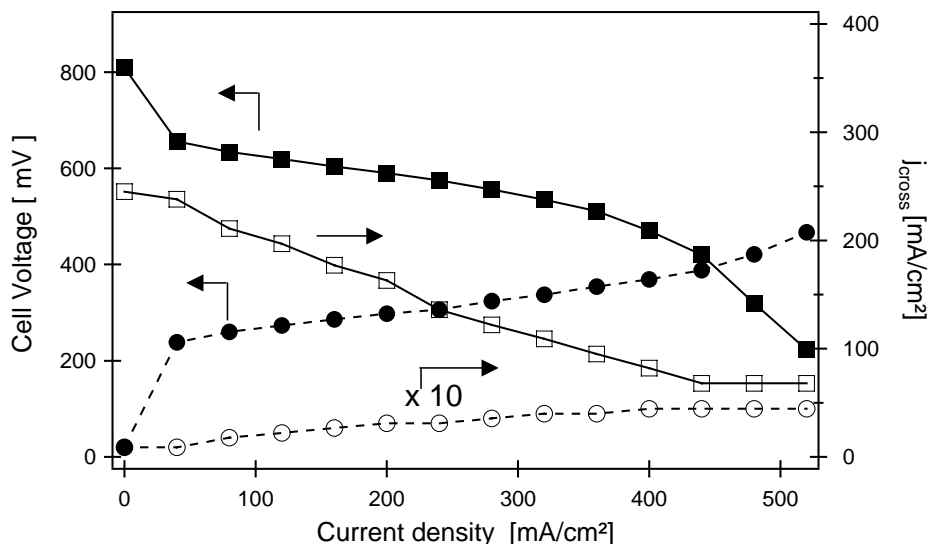


Fig. 2. DMFC performance curves for a MEA operated with air (square symbols) and the cell voltage recorded with a hydrogen evolving cathode (circles, same MEA). In the latter case, cell voltage corresponds to the anode potential. Full symbols: cell voltage and potential vs. current density. Open symbols: methanol permeation vs. current density (measured with a CO_2 sensor). Cathode flow is 4 l min^{-1} air and 0.3 l min^{-1} of hydrogen gas, Nafion® 105, 1 mol l^{-1} methanol (4 ml min^{-1}); cell temperature: 110°C . Anode: unsupported 5.4 mg cm^{-2} Pt–Ru, 2.5 bar pressure (outlet). Cathode: unsupported 6.3 mg cm^{-2} Pt, 4 bar pressure (outlet).

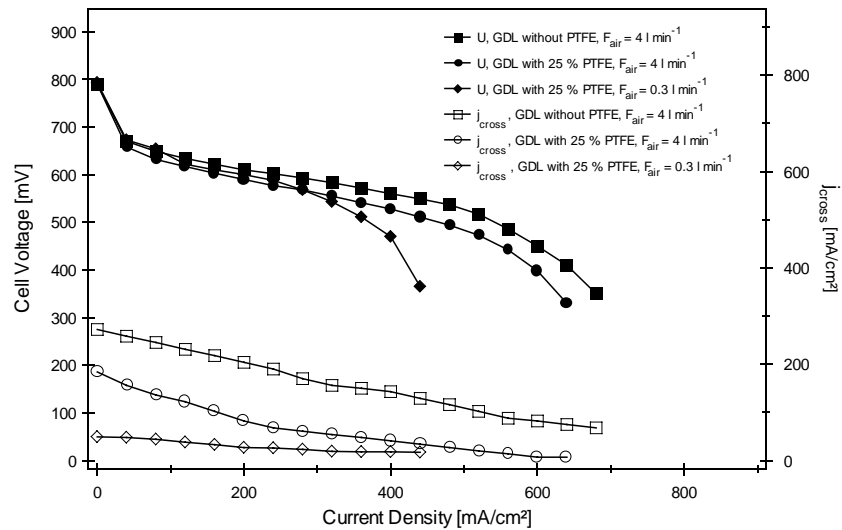


Fig. 3. DMFC performance curves for MEAs with different anode structures without and with PTFE in the GDL and different air flows at the cathode. Cell temperature 110 °C, Nafion® 105, 1 mol⁻¹ methanol (4 ml min⁻¹). Anode: unsupported 5.4 mg cm⁻² Pt–Ru, 2.5 bar pressure (outlet). Cathode: unsupported 6.3 mg cm⁻² Pt, 4 bar pressure (outlet).

properties of the electrode like a higher porosity. We can conclude from our results and MEA preparation procedures that the CO₂ permeation rate is insignificant and therefore a correction to the measured CO₂ rates at the cathode is not required.

3.2. Importance of electrode structure

In the measurement of Fig. 3, different anode structures with high performance are compared. The conventional anode structure without PTFE in the GDL exhibits the highest power densities at, e.g. 0.5 V. The DMFC with anode structures in which the diffusion layer was highly hydrophobic (25 wt.% PTFE) exhibit somewhat lower power densities. Again, the methanol permeation rate diminishes for all *U–I* curves with increasing current density since the conversion of methanol at the anode causes a decrease in the concentration gradient from anode to cathode.

A changed anode structure by introducing a high degree of hydrophobic components like PTFE reduces the methanol permeation. A possible explanation is that methanol is oxidized more efficiently at the anode due to the formation and stabilization of gas bubbles in the active area. As a consequence the methanol concentration gradient across the membrane is reduced. However, this explanation has to be taken with caution since the complex structure of the diffusion electrode may obscure the relationship between structure and mass transport. A recent publication by Nordlund et al. [16] found that adding PTFE has a positive effect on the performance of DMFC. We consider the results of Nordlund et al. to be in agreement with our results although a minor decrease in performance is observed in Fig. 3 with electrodes containing PTFE at a high air flow rate of 4 l min⁻¹. At lower flow rates of 0.3 l min⁻¹, a much more stable operation compared to PTFE-free electrodes is found. This oper-

ating condition is more comparable to the oxygen flow rate of 150 ml min⁻¹ used by Nordlund et al. These authors suggest that the PTFE improves gas formation in the electrode giving rise to improved mass transfer in the liquid phase.

Another important factor for methanol permeation is the air flow rate at the cathode. In Fig. 3, a lower air flow leads to much reduced methanol flow through the membrane consistent with the pervaporation function of the membrane. In pervaporation measurements of Nafion membranes in the absence of electrodes and electrochemical reactions, it is found that the permeation rate of aqueous methanol solutions is proportional to the inert gas flow rate (N₂ flow) [19]. Concurrently with the decrease in air flow rate, a reduced power density results. Nevertheless, an operation at reduced flow rates is advantageous regarding system efficiency. Although the MEAs which exhibited a reduced methanol permeation attain inferior power density, their system efficiency is higher because of the better fuel utilization. It has been reported that if the anode is sufficiently active to oxidize methanol electrochemically to CO₂ at a rate comparable to the supply of methanol, the concentration gradient and concurrently the methanol permeation drops to negligible levels [20]. Our results show that it is indeed possible to reduce the methanol permeation to negligible values at high current densities. However, a low to negligible methanol permeation for all current densities and the whole voltage–current–density curve was only achieved with low air flow rates at the cathode. Operation of the cell under conditions of high power densities of >250 mW cm⁻², e.g. at high temperatures and high cathode air flows of 4 l min⁻¹, are associated with high methanol permeation rates especially at higher cell voltage in the range of 800–600 mV.

Fig. 4 displays the dependence of the power density at 0.5 V cell voltage as a function of air stoichiometry at the cathode. The dependence on λ_{air} is shown for three different

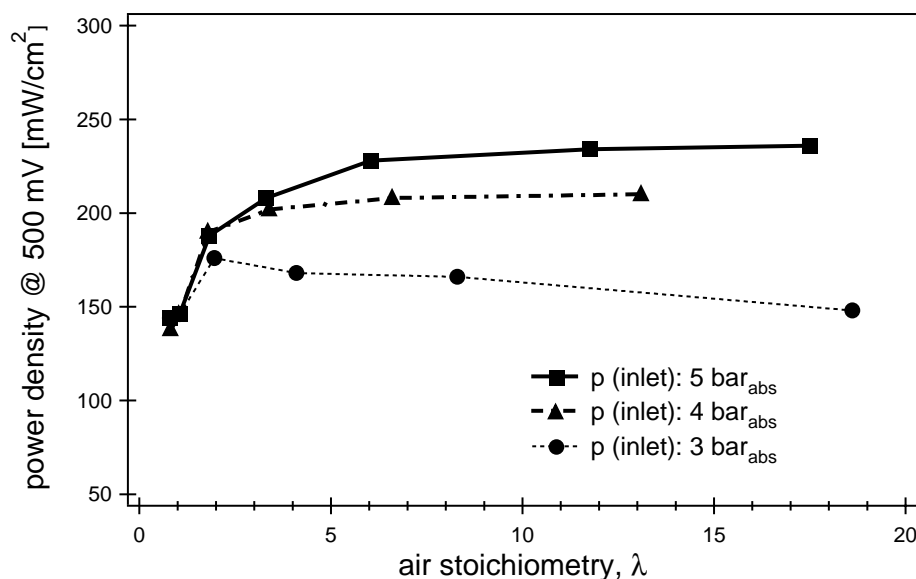


Fig. 4. DMFC power density at 500 mV cell voltage as a function of air stoichiometry at different cathode pressures. Hydrophobic GDL, cell temperature: 110 °C, Nafion® 105, 1 mol l⁻¹ methanol (4 ml min⁻¹). Anode: unsupported 5.4 mg cm⁻² Pt–Ru, 2.5 bar pressure (outlet). Cathode: unsupported 6.3 mg cm⁻² Pt. Lines are guides to the eye.

cathode pressures (■ for 5 bar, ▲ for 4 bar and ● for 3 bar absolute pressures). An interesting result is that the dependence of power density on stoichiometry is stronger for higher cathode pressures and only with 5 bar power densities over 200 mW cm⁻² were obtained. For the lowest pressure (3 bar) investigated, stable operation of the DMFC was possible at stoichiometries as low as $\lambda_{\text{air}} = 2$ maintaining a power density of about 150–175 mW cm⁻². A stable operation at low air stoichiometries was possible when using a hydrophobic anode gas diffusion layer. The MEAs with the standard gas diffusion layer showed a more unstable performance at low air stoichiometries in the range between $\lambda = 1$ and 2. At low air flow rate the methanol permeation is reduced. This can be detected independently in a pervaporation set-up for membranes where the amount of gas or permeate through Nafion membranes measured by gas chromatography strongly increases when the inert gas flow rate is increased [19].

3.3. Performance versus noble-metal loading

Precious metal alloys in the form of nanoparticles (2–5 nm) supported on carbon of high surface area are the most commonly employed catalysts in fuel cells. There are reports in the literature on both supported and unsupported catalyst compositions (Pt black catalyst) and Fig. 5 shows the influence of reducing the loading of unsupported catalyst at the cathode and one comparative measurement with carbon-supported catalyst (Pt–C) on the performance of DMFCs. As can be seen in Fig. 5 the reduction of noble metal loading in the cathode leads to a concurrent decrease in performance. The lowering of performance is gradual down to about 2 mg cm⁻². The decrease in open circuit

cell voltage of about 25 mV mg⁻¹ cm² may indicate a more pronounced mixed potential formation at the cathode when lowering the Pt loading. However, when the noble metal loading is reduced from 2 to 1 mg cm⁻², a decrease of the open cell voltage of about 200 mV is detected. Furthermore, the performance is drastically diminished by about 300 mV. This strong negative influence of the reduction of the loading from 2 to 1 mg cm⁻² cannot be simply due to the further reduction in catalytically active surface area. Two essential properties of the electrode are affected when reducing the unsupported catalyst loading to lower values. One property which may be affected is the electronic conductivity of the electrode. Secondly, the thickness of the electrode is altered considerably when varying noble-metal loadings.

The electronic conductivity is especially important in the direction normal to the membrane surface since this property of the electrode also determines catalyst utilization as well as iR losses. The conductivity parallel to the electrode surface is not so important as long as a diffusion layer with adequate electronic conductivity is used. However, it is very difficult to measure the conductivity in the direction normal to electrode surface accurately due to the small thickness of this layer. If we assume that the layer is isotropically conductive we can use the in-plane sheet resistivity as a measure of this property. The in-plane sheet resistivity can be measured relatively accurately with impedance spectroscopy in a dry state of the MEA (in the dry state the membrane resistance is in the order of 9 kΩ and therefore this resistance does not interfere with the determination of the electrode resistance). Although we have not investigated all MEAs used in Fig. 5, we find a dependence of the sheet resistivity on the loading of unsupported catalysts which were similarly

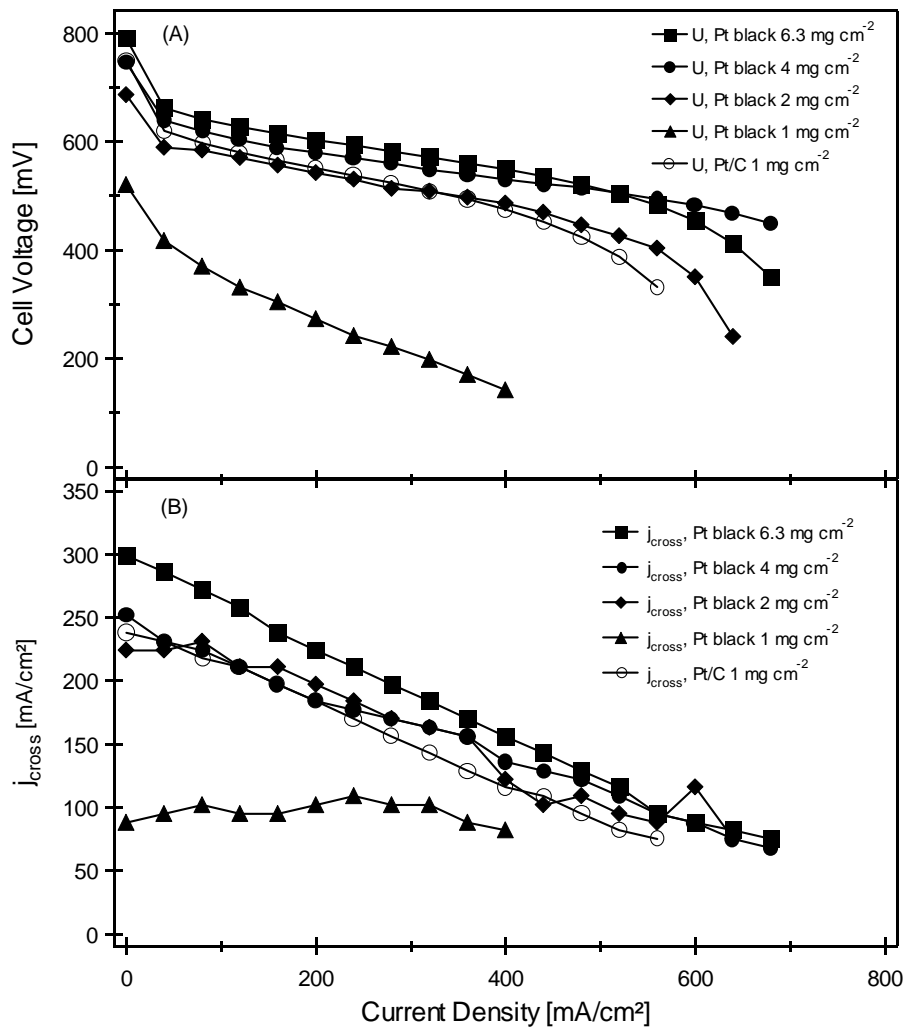


Fig. 5. (A) DMFC performance curves for MEAs with different cathode catalyst loadings of unsupported (full symbols) and supported (open symbols) catalysts. (B) Permeated methanol expressed in terms of current density (j_{cross}) for MEAs with different cathode catalyst loadings of unsupported (full symbols) and supported (open symbols) catalysts. Cell temperature: 110 °C, Nafion® 105, 1 M methanol. Anode: unsupported 5.4 mg cm⁻² Pt–Ru, 2.5 bar pressure (outlet). Cathode: cathode flow is 41 min⁻¹ air, 4 bar pressure (outlet).

prepared. An increase of the sheet resistivity from about 3.5 Ω/square for a loading of 2 mg cm⁻² to 6.3 Ω/square for a loading of 1 mg cm⁻² is observed. If the electronic conductivity is important for the performance, the use of carbon supported catalyst should reduce the influence of decreasing the cathode noble metal loading. Carbon supported catalysts have the advantage that the loading can be reduced without a concurrent decrease of electronic conductivity of the electrode.

However, a second aspect is that the use of carbon supported catalyst with a much lower bulk density is associated with significantly higher thickness of the active layer and the thickness of the electrode is an important parameter for the cell performance. The thickness of the electrode made with supported catalysts plays an important role in the mass transport of the fuel cell. A thicker electrode may lead to a higher mass transport resistance but, on the other hand, may also be of advantage at the

cathode, since mixed potential formation may be avoided to some extent. In a thicker electrode not all catalyst particles may be influenced by the permeated methanol which is converted to CO₂ in the vicinity of the membrane interface.

An additional measurement with 1 mg cm⁻² of carbon supported catalyst at the cathode and the corresponding methanol permeation rates (○) are shown in Fig. 5A and B. The MEA with the carbon supported catalyst exhibits a somewhat lower power density compared to a high-loaded MEA. This MEA even shows similar performance to the curve with 2 mg cm⁻² at lower current density and a loss of about 20 mV at higher current densities. Also, the methanol crossover rate is similar to the MEAs with unsupported catalyst. These results support the conclusion that besides the catalytic active area in the MEA other properties of the electrode like electronic conductivity and thickness of the electrode may be important factors influencing the performance

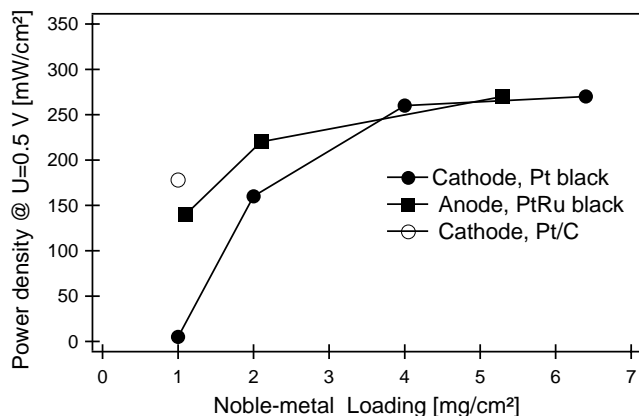


Fig. 6. DMFC performance at 0.5 V for MEAs with different cathode and anode catalyst loadings of unsupported catalysts (Pt black, Pt–Ru black) and with carbon-supported cathode catalyst (Pt–C). Variation of anode loading with constant cathode loading of 6.4 mg cm^{-2} . Variation of cathode loading with constant anode loading of 5.2 mg cm^{-2} . Cell temperature: 110°C , Nafion[®] 105, 1 M methanol (41 min^{-1}). Anode: 2.5 bar pressure (outlet). Cathode: cathode flow is 41 min^{-1} air, 4 bar pressure (outlet).

at reduced catalyst loading. Essentially, the use of carbon supported catalysts seems promising for achieving a lower noble-metal loading but maintaining other essential properties of the electrode. It is noted, however, that although unsupported catalysts have been shown to exhibit higher current densities for methanol oxidation, the mass specific catalytic activity is higher for supported catalysts [21]. Furthermore, supported catalysts offer a smaller crystallite size and relatively higher surface area compared to unsupported catalysts.

Fig. 6 shows the DMFC power density at 0.5 V cell voltage as a function of anode and cathode loading. It is

shown that it is possible to obtain high power densities in the range of 200 mW cm^{-2} at 0.5 V with significantly reduced catalyst loading. Only when the cathode loading is reduced from 2 to 1 mg cm^{-2} , a pronounced decrease was observed, which, however, was not present when using supported catalysts at the cathode. Therefore, the utilization of supported catalysts and their optimization in the electrode structure has the potential to a significantly reduced metal loading which will contribute to the cost reduction in DMFCs.

3.4. Stack design

In Fig. 7A, performance data of a 12 cell stack developed at ZSW is shown. The system includes the peripheral devices necessary for an autonomous operation, namely a blower for the air supply at the cathode and a methanol solution pump. These peripheral devices are included in the box below the stack. The stack is operated in the temperature range between 70 and 90°C using standard materials like Nafion[®] 105 and high noble metal loading of about 11.7 mg cm^{-2} per cell. 1 M methanol concentration is used. Produced CO_2 is separated in the fuel circulation tank and leaks through a small opening at the top. The temperature range is limited by the self heating properties of the stack. In contrast to the measurements in the single cells, the cathode is not pressurized. The power density at 0.5 V corresponds to $55\text{--}60 \text{ mW cm}^{-2}$. The inactive components of this stack are mainly graphite based, although some metallic components related to the gaskets have been introduced. At present, the improvement of the MEA materials is generally given a higher priority in the development of DMFC compared to the stack development [1,2].

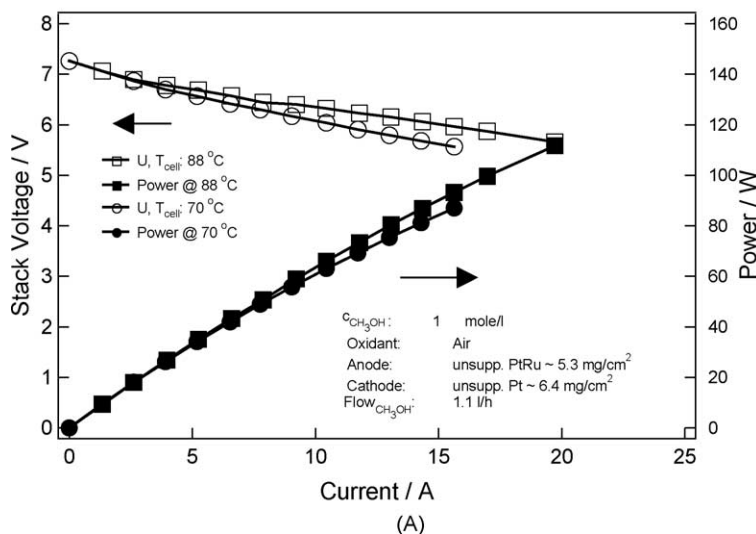


Fig. 7. (A) Performance curve of a 12 cell autonomous DMFC stack at different temperatures. Open symbols (full symbols) represent the stack voltage (power) vs. current density. (B) Image of the 12 cell autonomous DMFC system.

4. Summary and conclusions

The direct methanol fuel cell is an attractive option for numerous applications. However, this concept is hindered in its use by limitations which are associated with the non ideal properties of the standard materials presently employed. This is essentially the insufficient activity of the catalysts and the high methanol permeation through the membrane. In this contribution it is shown that it is possible to improve on these non ideal properties considerably by optimizing the electrode structure and choosing the operating conditions carefully.

The temperature dependent cell voltage versus current density curves show that the operating temperature has a significant influence on DMFC performance: the activity of the electrodes is increased at higher temperatures but concurrently the methanol crossover is also increased if the other parameters are held constant. In this respect, the electrode structure is of paramount importance: e.g. a hydrophobic anode backing leads to some decrease of power density, however, the decrease of methanol cross-over is significant which is associated with an increase in Faradaic efficiency. With such an optimized electrode structure, stable operation of the DMFC at lower air stoichiometry is possible. This was not the case for the standard anode backing.

A general conclusion that can be drawn from the results is that the noble-metal loading in DMFC can be reduced significantly while maintaining a sufficient DMFC performance: e.g. reducing the loading to 3.2 mg cm^{-2} (unsupported catalysts) and using a teflonized anode backing still yields power densities of ca. 150 mW cm^{-2} at 500 mV with the following operating conditions: 110°C , air flow: 1.25 l min^{-1} ($\lambda = 9.6$) or 130°C , air flow: 0.3 l min^{-1} ($\lambda = 2.3$).

The use of supported catalysts is promising and should result in further reduction of the noble-metal loading if electrode structures are optimized.

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