Influence of diffusion layer properties on low temperature DMFC

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Abstract

The effect of the diffusion layer on the performance and mass transport in a direct methanol fuel cell at ambient conditions is reported. Carbon cloths with variable Teflon contents and pore sizes, carbon paper and a metal wire cloth were investigated. Membrane-electrode-assemblies (MEAs) for direct methanol fuel cells (DMFCs) prepared after an in-house receipt are used, giving reproducible results after a pre-treatment involving polarisation with hydrogen and air. Long-term effects and methanol crossover were also briefly investigated. Adding Teflon to the diffusion layer leads to better gas transport, as gas and liquid transport takes place in different paths. Thus, the fuel cell power output is more stable. The same effect was seen with increasing pore size. Carbon paper is found not suitable as a diffusion layer for low temperature DMFC. The metal wire cloth yielded best performance giving $15.8 \, \text{mW cm}^{-2}$.
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1. Introduction

The direct methanol fuel cell is a promising power converter for a wide range of applications from small sensors and portable electronics up to stationary power plants. Low temperature operation and the use of liquid fuel make DMFC systems very simple, without the need for humidification and thermal management systems, fuel vaporiser or reformer. The use of liquid methanol as fuel provides high energy density and fast and convenient refuelling. Hence, the DMFC may become a viable substitute to batteries especially for portable electronics. Cell performance vary significantly with operating conditions. State-of-the-art power densities are in the order of $15 \, \text{mW cm}^{-2}$ for single cell passive systems [1] and up to $50 \, \text{mW cm}^{-2}$ for small stacks operating at higher temperatures [2].

However, there are some challenges associated with DMFCs as power converters. Compared to the hydrogen fed proton exchange membrane fuel cell (PEMFC), the anode oxidation kinetics of methanol are by far slower. Different reaction mechanisms have been proposed [3,4], and although no consensus about the correct reaction path has been reached, it is commonly recognised that intermediates such as carbon monoxide are adsorbed to the active catalyst sites, thus blocking further methanol oxidation. Binary catalysts such as PtRu are used to improve the reaction kinetics. With these catalysts the second metal forms a surface oxide or hydroxide in the potential range of methanol oxidation [5].

Another problem is related to the methanol permeation through the polymer membrane, commonly referred to as methanol crossover. Methanol has many similar physical properties as water, and since proton transport through the membrane is facilitated by water, this implies that methanol molecules also follow this path. Crossover increases with temperature and methanol concentration [6]. The effect of crossover is two-fold; the reduction in cell current as well as in cell voltage. Even at low methanol concentrations and ambient conditions, the cell voltage declines significantly due to a mixed potential at the cathode. There, methanol is directly oxidised with a corresponding reduction of oxygen. Thus, lowering the cell voltage resulting in a loss of power and methanol. Carbon monoxide produced during operation is adsorbed on the platinum catalyst surface, thus blocking further reactions. For all applications, and especially for portable applications, the use of high concentration methanol solution is favourable, as it gives the highest energy density. This increases the crossover, however.

The third major difficulty regarding DMFCs is related to the carbon dioxide evolution at the anode. According to the

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DMFC reaction equation, Eq. (1), one mole of gas is formed for every mole of methanol oxidised.

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \tag{1}$$
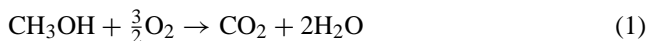
A direct methanol fuel cell providing 10 Ah produces about 1.4 l of carbon dioxide gas. The solubility of carbon dioxide in a methanol–water solution is very low (0.86 ml CO_2 per ml solution at 20 °C [7]), therefore, small gas bubbles will form. In the case of insufficient gas transport away from the anode catalyst surface, methanol access to the reaction sites will be hindered. Thus, the two-phase transport in the anode diffusion layer is a critical factor in DMFC research. The effect of Teflon content in the anode diffusion layer on cell performance has previously been investigated for higher temperature DMFCs. The optimal Teflon amount was found to be between 13 and 20 wt.% [8]. Metal wire cloths used as diffusion layers have also been tested with promising results [9].

Mass transport in the DMFC anode is a very complex subject. Methanol must be transported through the diffusion layer to the anode, where it is consumed. Carbon dioxide is produced on the catalyst surface, and to avoid blockage of the reaction area, it must continuously be removed, see Fig. 1. Thus, we are dealing with a two-phase counter current flow in a porous medium.

Mass is transported by diffusion from the high (c_i) to the low (c_i^0) concentration area. One dimensional diffusion is generally described by Fick's 1st law:

$$j = -D\frac{\partial c_i}{\partial x} \tag{2}$$

where j is flux per area (mol s^{-1} m^{-2}), D the diffusion coefficient (m^2 s^{-1}), c_i the concentration of specie i (mol m^{-3}) and x is the diffusion distance (m). Specie i diffuses through a substance, where its diffusion coefficient is D, from the high concentration side to the low concentration side. If the distance x (thickness of diffusion layer) and the concentration on both sides are known, the equation can be linearised:

$$j = \frac{D}{l}(c_i - c_i^0) \tag{3}$$

where l is the known distance, c_i and c_i^0 are the high and low concentration, respectively.

In the DMFC, D will be the diffusion coefficient of methanol in water, l the diffusion layer thickness, c_i the

feed methanol concentration and c_i^0 the concentration at the catalyst (anode) surface. D is given as 1.26×10^{-9} m^2 s^{-1} at 15 °C and infinite dilute solution [10]. l varies with diffusion layer (∼0.1–1 mm), c_i is often 2 M and c_i^0 varies with current density. When the limiting current is reached, methanol concentration on the reaction surface, c_i^0, is zero, and diffusive transport of methanol through the diffusion layer is the limiting process. Thus, Eq. (3) becomes:

$$j_{lim} = \frac{D_{MeOH/H_2O}}{l_{DL}} \times c_i \tag{4}$$

Since the concentration on the reaction surface is zero, this is the highest flux (mass transport) possible for this system, and therefore also the highest possible current. From the reaction equation (Eq. (1)) for the DMFC and, from [11]:

$$i_{lim} = nF \times j_{lim} \tag{5}$$

where i_{lim} is the maximal current and F the Faraday's number (96,485 C mol^{-1}). We get the following relationship between limiting current and the diffusion coefficient:

$$i_{lim} = nF \times \frac{D_{MeOH/H_2O}}{l_{DL}} \times c_i \tag{6}$$

Thus, when measuring the limiting current, the diffusion coefficient may be deduced, when the other parameters are known.

Since methanol transport occurs through a wetted diffusion layer and not a water film, some adjustments to Eq. (6) are needed. Diffusion in porous media means that transport will have to follow certain paths and pores. Longer diffusion distances and smaller areas are often lumped together in an effective diffusion coefficient, D_{eff}, [12]:

$$D_{eff} = \varepsilon \times \frac{D}{\tau} \tag{7}$$

where D is the original diffusion coefficient, ε the open void fraction (also called valid fraction) and τ is tortousity. The tortousity will account for longer distance traversed in the pores.

Carbon dioxide transport in the porous layer also affects methanol diffusion. If gas bubbles occupy whole pores, the methanol diffusion will be reduced due to a lower open void fraction in the diffusion layer. If small bubbles are present in the pores, they may cause motion and therefore forced convection of the liquid. Convective transport is much faster than diffusion, which gives a higher limiting current. The effects of gas evolution depend on gas evolution velocity, which again is dependent on current density, structure of diffusion layer, liquid flow and more. This makes quantitative determination of these effects very complicated. The two-phase flow pattern will depend on a number of factors:

- Whether or not the nucleation sites for the gas generation remains constant.
- The characteristics (morphology, density and composition) of the interphase between anode and porous medium.
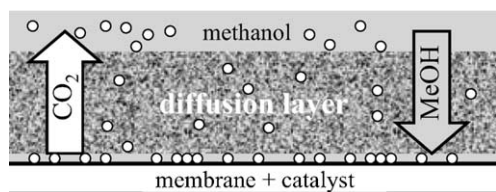

Fig. 1. Schematics of the two-phase transport in the anode diffusion layer in a DMFC. Methanol diffuses to the anode and is consumed during formation of carbon dioxide.

- The rate of gas generation (current density).
- The relative importance of capillary to viscous and gravity (and possibly inertia) forces.
- The possibility of snap-off of adsorbed carbon dioxide bubbles from the catalyst surface.

2. Experimental

The membrane-electrode-assemblies were prepared after an in-house receipt, involving pre-treatment boiling of the membrane (Nafion N117), applying the catalyst layer onto the membrane followed by hot-pressing and a cleaning procedure. Catalyst loading on both electrodes was $5\,mg\,cm^{-2}$, with Pt and Pt/Ru (1:1, a/o) on cathode and anode, respectively. To obtain reproducible results with the in-house made MEAs, they had to be pre-treated to reduce adsorbed oxides on the anode catalyst surface. This was made in the fuel cell by changing polarity twice and polarising the cell to 500 mV during hydrogen/air operation.

The test cell used in the experiments consisted of an in-house made MEA and diffusion layers sandwiched between two circular stainless steel flow field plates. The active surface area was $12.5\,cm^2$. Spot flow fields were used on both cathode and anode side. On the cathode side, all structures were 1 mm wide and 1 mm deep, anode channels were also 1 mm wide but 2 mm deep. With the chosen cell fixture, one could also vary bolt torque (cell housing) and MEA torque (pressure on MEA).

For the testing of diffusion layers with methanol, a pulse free pump (Cat Microdosing Pump HPLH 200-PF) was used to feed the water/methanol mixture to the cell. The MEAs were first conditioned at open circuit voltage for 5 min, polarised to 100 mV for 30 min and then left at open circuit voltage for another 30 min. Conditioning and all experiments were performed with $10\,ml\,min^{-1}$ 0.5 M methanol and $100\,ml\,min^{-1}$ air at ambient pressure. With 50 mV intervals polarisation plots were obtained from open circuit voltage to short circuit with a Bank Potentiostat Wenking Model HP 88.

Table 1 shows the properties of the diffusion layers that were tested for anode application. On the cathode side, GORE Carbel CL Gas Diffusion Medium was applied for all cell tests. Bolt (cell housing) torque and MEA torque were 3 and 1 Nm, respectively. Resistance in the cell was measured with a four-point measurement Hewlett-Packard, 4328 A milliohmmeter.

Both PEMFC and DMFC systems involve two phase transport. To enhance the gas flow, one can make the diffusion layer hydrophobic (e.g. by treating with Teflon), thus creating regions for free gas movement as routinely adopted in gas fed gas diffusion electrodes [8]. By varying the Teflon content, different levels of hydrophobicity can be obtained. Carbon cloths come in different weaves and coarseness. Type "A" is the most used diffusion layer in higher temperature DMFC [14]. This structure has both large and small openings, suitable for both liquid and gas transport, respec-

Table 1
Properties of diffusion layer tested [13]

Diffusion layer	Thickness (mm)	Weight (g cm^{-2})	Teflon content (wt.%)
Carbon Cloth A, from E-TEK, Inc.	0.35	0.12	0
Carbon Cloth A, from E-TEK, Inc.	0.35	0.14	15
Carbon Cloth A, from E-TEK, Inc.	0.35	0.16	30
Carbon Cloth B, from E-TEK, Inc.	0.65	0.22	0
Carbon Paper TGP-H-090 from Toray	0.26	0.49	0
Wire Cloth Heddle weave[a]	0.45	0.10	0

[a] Stainless steel wire cloth (5/110/60 VA, 107 mesh $\times$ 60 mesh in.$^{-1}$) from Filtertechnik GmbH Willy Spee.

tively. Carbon paper has a structure with pore sizes between 20 and $50\,\mu m$ but with large proportions of blocked passages. Because of this it shows some hydrophobic properties. Different thickness are available from 0.09 to 1.5 mm, but these are mostly used as gas diffusion media.

A longer term experiment was performed to investigate the direct methanol fuel cell degradation. The standard test procedure was carried out, but when obtaining the polarisation plots for methanol oxidation, the cell current was read for 15 min at each voltage. After additionally 13 h at 100 mV, the polarisation curve was obtained again to observe possible changes. To determine the methanol crossover, the carbon dioxide content in the cathode outlet was measured with an Infrared (NDIR)-Spectrometer URAS 10 E.

3. Results and discussion

The in-house production of reproducible MEAs was first seen successful after performing a cleaning procedure on the hot pressed MEAs. This cleaning procedure involved changing polarisation during hydrogen/air fuel cell operation. An oxide layer seemed to have been adsorbed to the anode surface, which was removed by cathodic polarisation of the anode. In order to investigate the catalytic properties of the MEAs, hydrogen, instead of methanol, was used as anode feed. This gives a more correct picture of the activity of the catalyst, as no or very little transport limitations are observed during hydrogen operation.

SEM-photos of the in-house prepared MEAs show a porous and uniform anode surface, see Fig. 2a. This also indicates a large three phase area for the electrochemical reactions. At the cathode side, equally fine surfaces were seen. Catalyst layer thickness is almost $10\,\mu m$, and it seems to be uniform over the whole surface, see Fig. 2b. On the basis of the SEM-photos, the irreproducibility observed during the first measurements did not seem to be a result of non-uniform catalyst distribution or inhomogeneous grain sizes in the MEA.
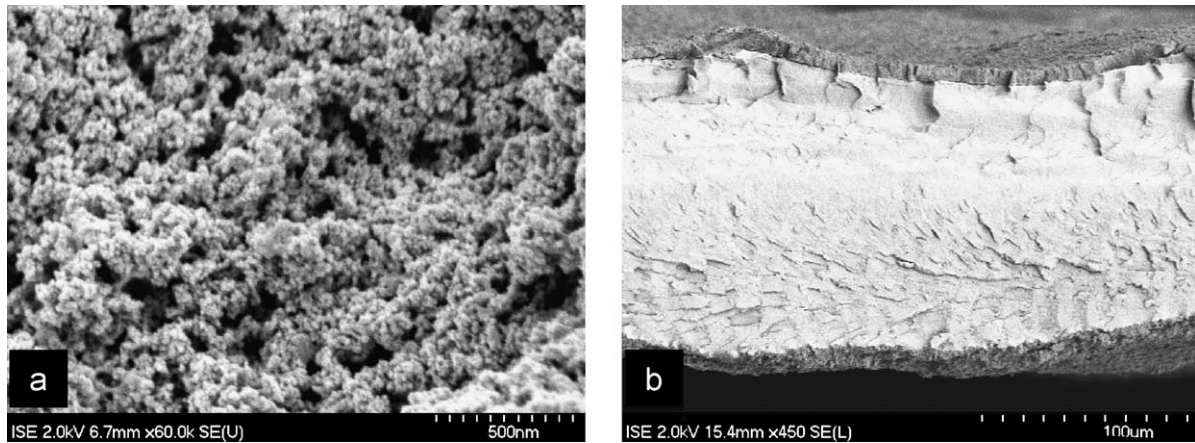
Fig. 2. SEM photos of the MEAs. (a) Anode surface and (b) cross-section.

Since hydrogen diffusion is extremely fast, due to its small molecular size, it is most probable that oxide adsorption on the active catalyst sites was limiting the fuel cell performance, and not a diffusion barrier. After the change of polarity procedure, the results were not only reproducible, but also 10 times better than before, see Fig. 3. For low temperature operation, it seems very important that the hotpressed MEAs for DMFC are properly activated before use. In contrast to high temperature operation, oxide layers at the anode must be removed.

Before each methanol experiment, this oxide removal procedure was performed on the MEA in the fuel cell. This way a quality control was achieved. The resistance in the fuel cells were measured to be between 30 and 40 mΩ, varying mostly due to the different diffusion layers. The low and reproducible cell resistance also indicates that the membrane conditioning and humidification during measurements were successful.

In Fig. 4, the low open circuit potentials with methanol feed can be observed. Compared to the theoretical value

1200 mV, 500 mV seems inadequate. The reasons for this are mainly methanol crossover, as well as concentration and temperature effects. Considering the open circuit voltage model presented by Sundmacher and Scott [6], an expected value could be around 500–550 mV at these conditions, which is in agreement with our measurements. The rapid voltage decline of about 150 mV from open circuit voltage to 5 mA cm^{-2}, corresponds to the activation overvoltage. This high activation loss indicates that the catalyst either has an unfavourable structure or composition. Poor contact between catalyst material and membrane can also be a problem, but this would probably not influence much at such low currents. The above mentioned features were seen to a similar extent in all experiments, and did not contribute to errors in the measurements.

When the current increases, carbon dioxide transport at the anode influence on the performance. Bubbles are formed at the catalyst surface, thus blocking further oxidation. As the bubbles grow, these blocked areas become larger, until the bubble is released and transported through the diffusion
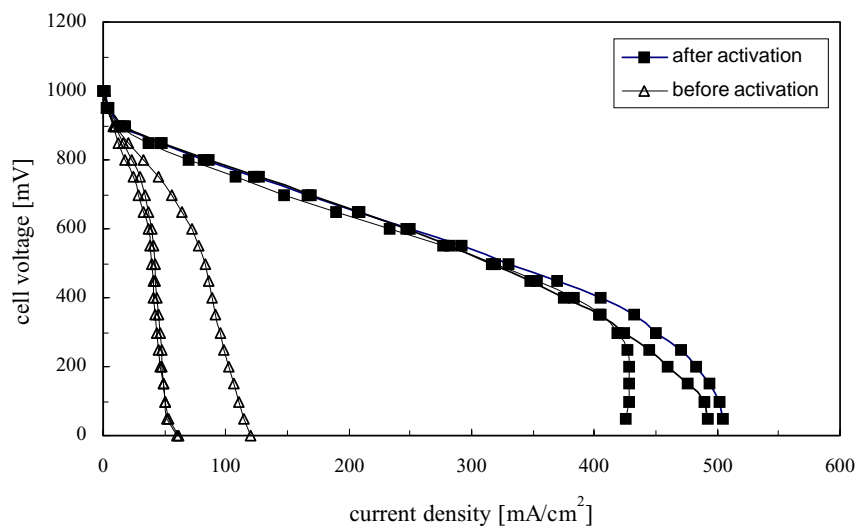

Fig. 3. Polarisation curves before and after activation. Removing adsorbed oxides from the anode surface gave higher and reproducible performance of the MEAs.
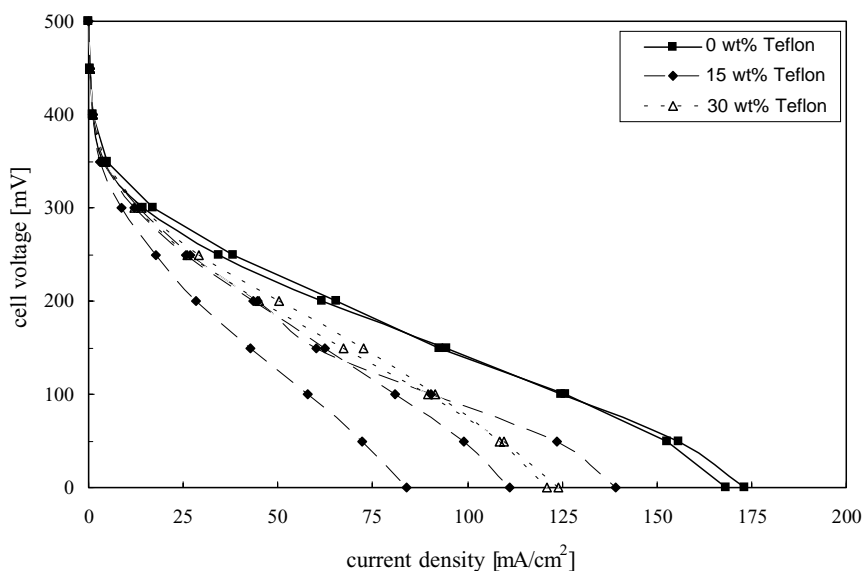
Fig. 4. Polarisation curves for diffusion layers with variable Teflon contents.

layer. Then the available reaction area increases, which also means that the current increases. This continuous forming and breaking causes the oscillating current density. As described in the introduction, diffusion layer properties also affect this process, either by enhancing or impeding carbon dioxide transport.

Carbon cloth diffusion layer type A was tested with different amounts of Teflon, see Fig. 4. Since the anode mass transport involves both gas and liquid phase, the influence of wet proofing in the diffusion layer was investigated. Plain cloth without wet proofing was tested first. The current during measurements was observed oscillating 1–2% around a constant value. The high current density indicates good methanol transport to the anode, but due to the unstable current, the carbon dioxide removal does not seem to be so ideal. In the outlet tube from the anode, large bubbles were observed leaving the system. Since no bubbles were entering the system on anode side, this had to be the produced carbon dioxide. This did not come in small uniformly sized

bubbles, but rather unsystematically in larger clusters. Large bubbles could be formed on the catalyst surface, thus lowering the available reaction surface, before they finally exit through the diffusion layer and out of the cell. Then the current rises because of the released active area. Since the cell material was partly transparent, it would have been possible to see if the cell construction was the bottleneck. No signs of this were observed, indicating that carbon dioxide evolution on catalyst surface and transport through the diffusion layer caused the unsteady current.

According to theory, making the diffusion layers hydrophobic should enhance gas transport. In Fig. 5 the difference between an untreated and treated diffusion layer is shown. When liquid and gas are transported in different paths, large and small pores, respectively, carbon dioxide removal will be more uniform. Thus, also giving a more stable current. This is what was seen when diffusion layers with 15 wt.% Teflon was tested. Comparing with no wet proofing, current oscillation was reduced to an insignificant
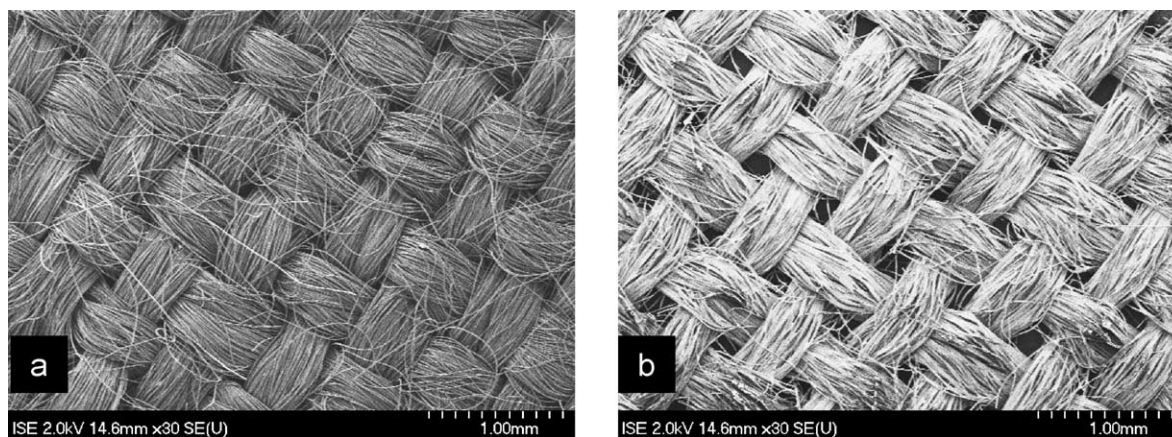

Fig. 5. SEM photos of untreated (a) and 15 wt.% Teflon treated (b) diffusion layer.

level. Although the current densities were lower, they were far more stable. Opposed to previous observations, small bubbles now left the fuel cell uniformly. This indicated that smaller bubbles of carbon dioxide gas were formed, before they were transported through the diffusion layer and out of the system.

The striking feature seen in the 15 wt.% Teflon measurements is the very irreproducible results. A variation of more than 50% in current densities at short circuit is much compared with the first measurements. The plots are homogeneously distributed between 84 and 139 mA cm^{-2}. Since reproducible results were seen on most other measurements, the diffusion layers and/or the wet proofing procedure could have caused it. When measuring the 30 wt.% wet proofed diffusion layers, very reproducible results were again obtained. Current densities were lower than plain cloth, but the stable current characteristics was distinct during measurements. Low current fluctuations were observed and small bubbles were now leaving the cell in an orderly manner. Wet proofing seemed to enhance stable carbon dioxide transport through the diffusion layer. Adding Teflon to the diffusion layer increases the electrical resistance. For the tested layers, an increase of approximately 10 and 15% in resistance was seen from the plain cloth to 15 and 30 wt.%, respectively. Comparison of the slopes of the different cloths supports these measurements. Steeper polarisation curves indicate higher resistance, thus resulting in lower currents.

The results of testing with wet proofing indicated that it could be advantageous also to operate with larger pores in the anode diffusion layer than in the Carbon Cloth A. This seemed to enhance the two phase transport at the anode side. Carbon Cloth B is somewhat coarser, with pore sizes about twice that of Carbon Cloth A, see Fig. 6. It is also nearly
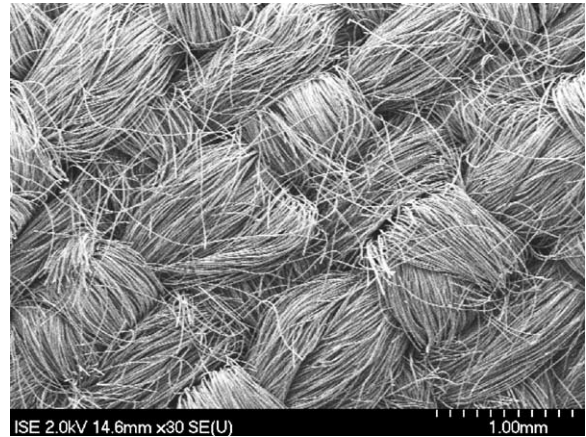

Fig. 6. SEM photo of Carbon Cloth B plain weave.

twice as thick, 0.65 mm, which means longer diffusion paths both for carbon dioxide and methanol.

Polarisation curves for Carbon Cloth B compared to Carbon Cloth A, are shown in Fig. 7. As seen in the first comparisons, the differences in current densities occur mostly at very low potentials. This is obvious, as the high potential region is activation and resistance controlled, and gives more information about the MEA than the diffusion layer. Not until the currents are high enough to create some mass transport and resistance limitations, differences between the diffusion layers are seen.

Current densities are lower for Carbon Cloth B than for Carbon Cloth A. As previously stated, Carbon Cloth B is thicker, and this leads to lower methanol concentration at the anode surface, since the diffusion distance is longer and thus slower. As current density is dependent on surface concentration, this decreases the performance. The larger pores
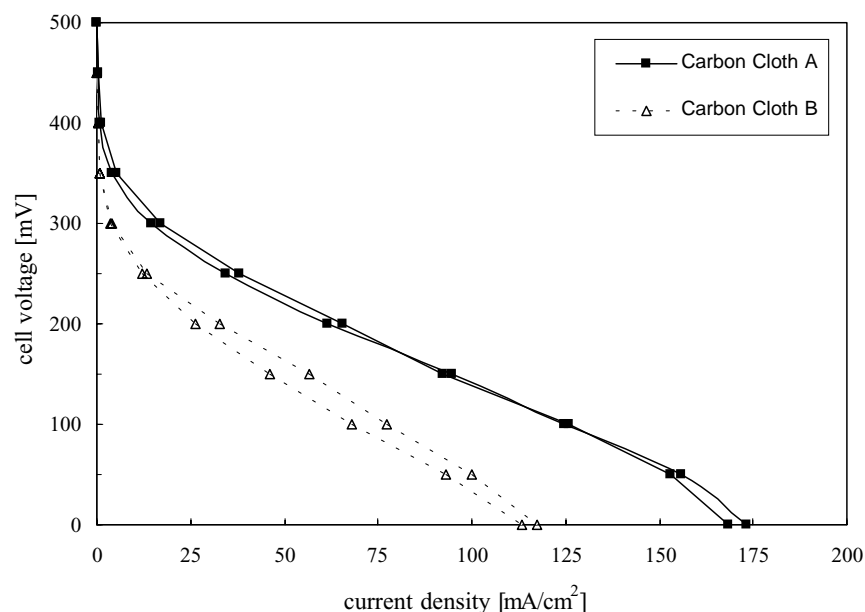

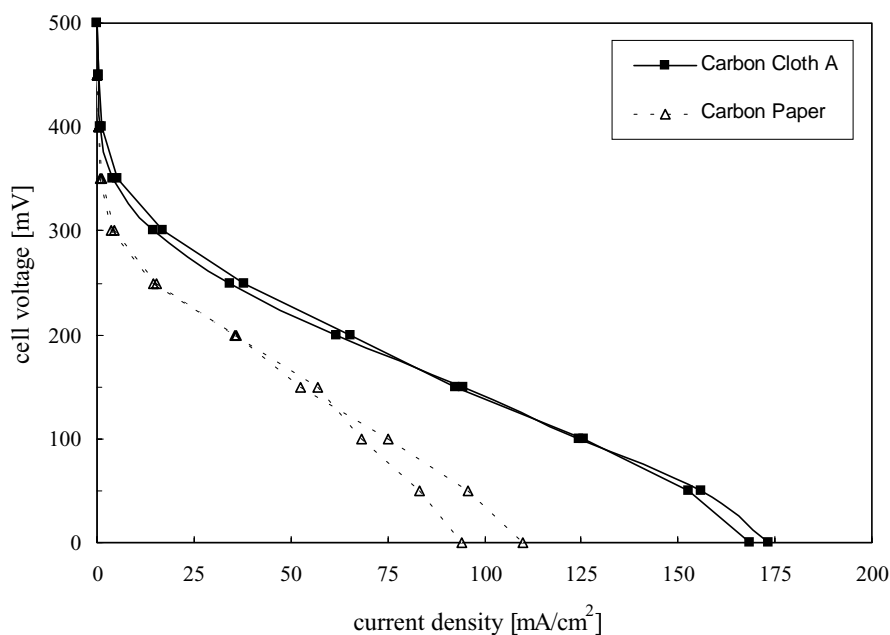Fig. 7. Polarisation curves for Carbon Cloth B and Carbon Cloth A.

Fig. 8. Polarisation curves for Toray Carbon Paper 260 and Carbon Cloth A.

do not seem to compensate for methanol transport in power output, but it supports the stable operation results from the wet proofing tests. Both at the anode outlet, where small bubbles were seen, and in the stable current it can be seen that also larger pores are advantageous for uniform gas removal. Larger pores are favourable for stable currents, but it also means longer average distances for electrons to move in the catalyst layer, until a contact between diffusion layer and catalyst is found. Thus, the overall resistance increases.

The literature indicates that carbon paper is not suited as anode diffusion layer for higher temperature DMFC [14]. This was nevertheless tested to investigate possible differences at lower temperatures and to confirm the results. Fig. 8 shows two polarisation plots obtained. As seen, the current densities are of the lowest achieved, and in addition the currents were very unstable. At short circuit, it fluctuated with over 10% during measurements. The carbon dioxide bubbles are closed in the Toray paper structure, thus clogging methanol access.

Another special feature during operation of the DMFC with Toray Paper as anode diffusion layer was the very slow response to potential changes. From the SEM-photo of the Toray Carbon Paper 260, see Fig. 9, the totally different structure from carbon cloths can be seen. Small pores and areas are almost totally blocked, which hinders the methanol transport. The same phenomenon occurs as earlier described. Carbon dioxide gas bubbles being trapped between the MEA and the diffusion layer until large clusters of bubbles force their way out, causing the unstable current.

None of the above tested diffusion layers were especially made for direct methanol fuel cells. Conveniently, they are used because of their wide spread application in gaseous fuel cells, and to some extent thereafter modified for liquid op-

eration. The metal wire cloth tested was especially designed for filtration purposes with good liquid distribution over the whole surface, see Fig. 10.

The metal wire cloth showed the highest power performance of all tested diffusion layers. Current is higher at all potentials and almost $190 \, mA \, cm^{-2}$ at short circuit. Thus, the results are promising. Compared to the carbon cloths, the pores are smaller and the metal wire cloth is somewhat thicker, see Fig. 11. This does not agree with the advantageous properties found earlier. For the carbon based diffusion layers, larger pores and thinner cloth performed best, but other parameters also influence, i.e. MEA-diffusion layer contact, resistance, wetting properties and the difference between steel and cloth surface properties.

Resistance was lower than with all the carbon materials, about 10% lower than Carbon Cloth A. This means that by
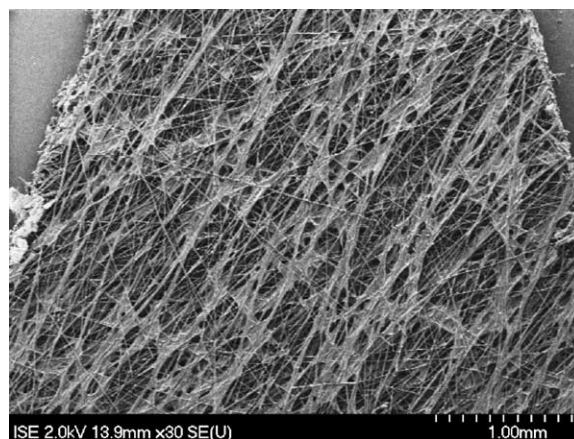

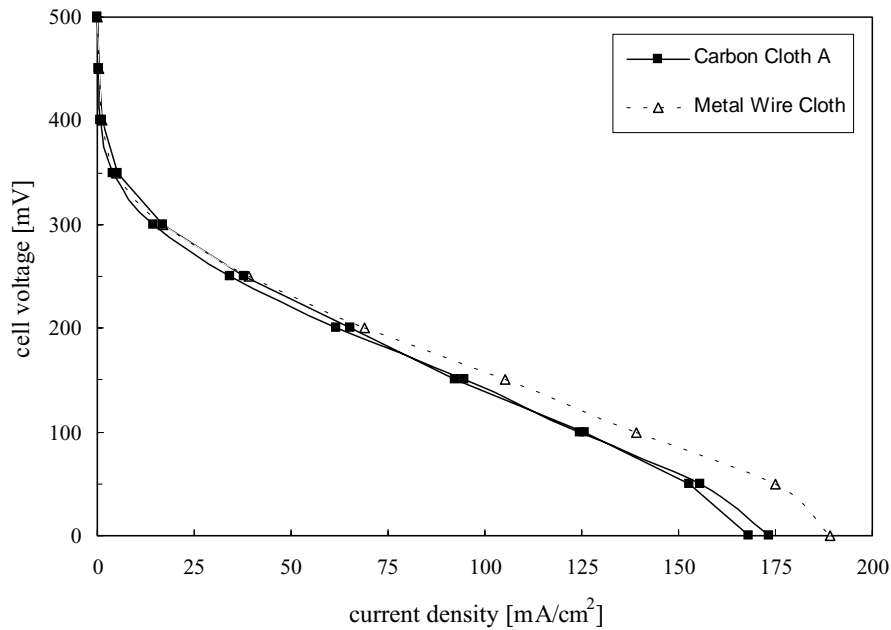Fig. 9. SEM-photo of Toray Carbon Paper 260.

Fig. 10. Polarisation curves for metal wire cloth and Carbon Cloth A.

choosing metal wire cloth instead of wet proofed carbon cloth, over 20% reduction in resistance can be achieved. At the same time, the current was as stable as with the Teflon treated cloths. Although there are not the same separate paths for gas and liquid transport, it seems that this metal weaving shows equally good properties regarding mass transport. Response to potential changes was also good with this metal wire cloth, both with hydrogen and methanol as feed.

Carbon Cloth A with 30 wt.% wet proofing and Carbon Cloth B were the diffusion layers with the most stable operation during these measurements. The differences are not large at high potentials and low current densities, mostly because diffusion layer properties do not influence the performance much. But at around 150 mV the differences both in current densities and fluctuations appear to be large. At short circuit and maximum current, some diffusion layers show

Fig. 11. Photo of metal wire cloth structure.

signs of mass transport problems. Especially Carbon Paper, but also Carbon Cloth B and Carbon Cloth A with 30 wt.% wet proofing were not able to provide the same amount of methanol as Carbon Cloth A and the metal wire cloth.

It was also seen that current density is inversely proportional to the resistance, but it cannot be the only cause of the differences observed. At very low potentials and high currents, mass transport through the diffusion layer interferes with performance. Even though no real limiting currents were seen, it does not mean that mass transport does not have an effect on the system. If all gas bubbles were to be removed instantly from the catalyst surface, currents would be higher due to larger available reaction area.

Judging from the metal wire cloth test, this has the most suited properties for low temperature DMFC operation, considering both power output and stability. Maximum power was near $16\,\mathrm{mW\,cm^{-2}}$, see Fig. 12. Current densities were very stable, even at low potentials. It was also observed that Carbon Cloth A with 15 wt.% wet proofing showed some of the same properties.

As a test of both MEAs and diffusion layers degradation a long-term test was performed. The current density trend is shown in Fig. 13. A constant drop of nearly $3\,\mathrm{mA\,cm^{-2}\,h^{-1}}$ was observed during almost the whole 13 h. period. The first 2 h are somewhat more unstable and an indication of current stabilising can be seen in the end. If the degradation continues constantly with $3\,\mathrm{mA\,cm^{-2}\,h^{-1}}$, the performance will be reduced to the half after only 20 h operation.

At 100 mV and around $100\,\mathrm{mA\,cm^{-2}}$ we have previously seen some effect of mass transport limitations in the anode diffusion layer. It is very unlikely that mass transport equilibrium in the diffusion layer has not been established. Then it is most likely that the decrease in current is due to
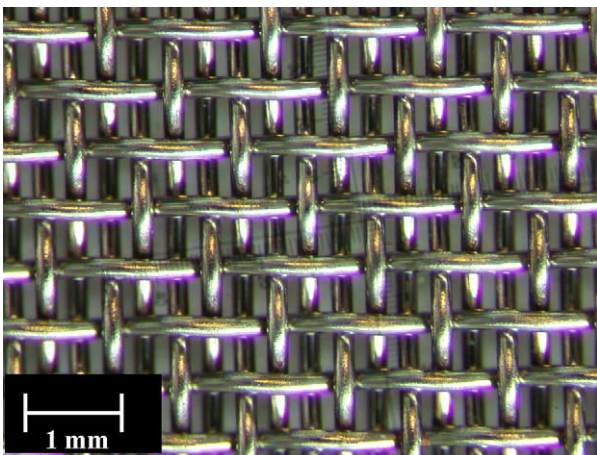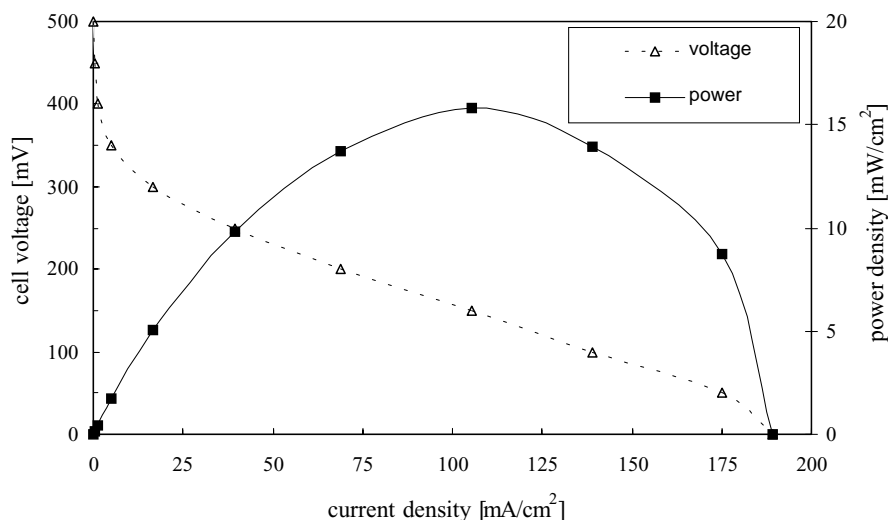
Fig. 12. Voltage–power plot of the metal wire cloth.

degradation of the MEA catalyst. On the anode side, intermediates such as formic acid, methyl formeate, formaldehyde, methylal and carbon monoxide and the product carbon dioxide can poison the catalyst. This could explain the constant decline, as less active sites are available for methanol oxidation. Methanol crossover could also be involved in this degradation. All or most of the methanol that diffuse through the membrane, is oxidised at the cathode as well. Since there also is a platinum catalyst there, there will most certainly be problems with carbon monoxide adsorption. In addition the same intermediates mentioned before are formed here as well. Both degradation of anode and cathode catalyst is possible, but due to the low crossover at these conditions, it is most likely that the Pt/Ru catalyst mixture on the anode was

not sufficiently resistant towards the poisoning by the intermediate products. The polarisation curves obtained before and after the 13 h test were almost identical. This indicates that the deteriorating effect was not permanent.

The measurements of methanol crossover showed that 0.4–0.6 vol.% of the outlet at cathode side was carbon dioxide. Assuming that all methanol is oxidised this corresponds to a 3–5 mA current, totally (0.24–0.40 mA cm^{-2}). According to these data there is no problem with methanol crossover at these conditions. Taking into consideration the low open circuit voltage and power output, the crossover value was so low that it indicates that not all methanol on cathode side was oxidised to carbon dioxide. Without crossover the performance should be higher.
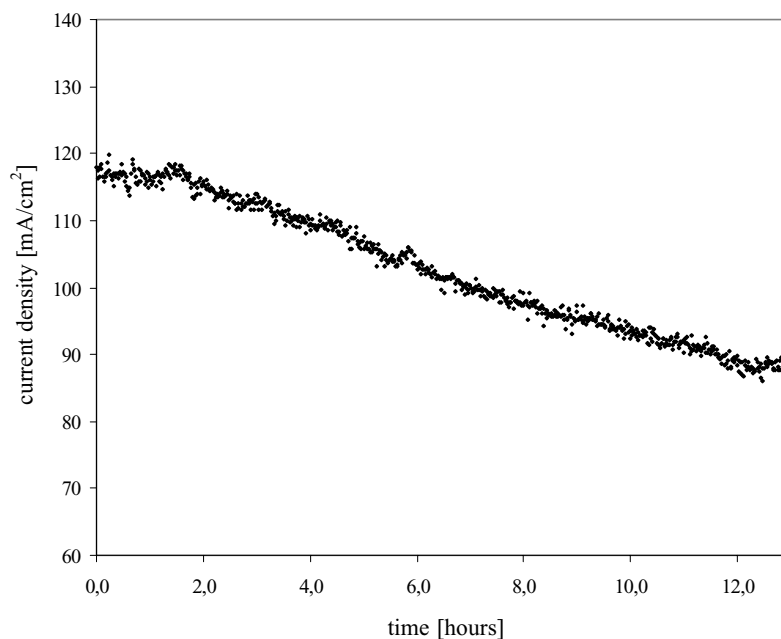

Fig. 13. Current density decrease during 100 mV voltage operation.

4. Conclusion

The investigated production and preparation procedure for MEAs with binary catalysts gave reproducible results. During operation at ambient conditions, it is however crucial that a proper cell activation procedure is carried out, as oxide layers cover the catalyst surface. This research has also shown that liquid fed direct methanol fuel cells are highly influenced by the diffusion layer characteristics. Properties such as pore size, Teflon content (wet proofing) and diffusion layer thickness control the two phase transport on the anode side. Optimisation of these properties is especially important at high current densities, where large amounts of carbon dioxide are produced at the anode. Effective removal of carbon dioxide is crucial for stable and high power output operation.

Adding Teflon to the diffusion layer leads to better gas transport, as gas and liquid transport takes place in different paths. Thus, the fuel cell power output is more stable. The same effect was seen when increasing the pore size from about 50 μm, in E-TEK's Carbon Cloth A, to some 200–300 μm in Carbon Cloth B. Carbon paper, with pore sizes between 20 and 50 μm and large proportions of blocked passages, is found not suitable for low temperature DMFC. A metal wire cloth showed best performance giving 15.8 mW cm^{-2} at 150 mV, and it also possessed properties that enhanced stable operation.

Only small amounts of carbon dioxide were detected at the cathode side outlet, indicating either that only small amounts of methanol diffuse through the membrane at these operation conditions, or that little of this is oxidised. Long-term test of the MEAs indicated that intermediates and/or products from the methanol oxidation poison the catalyst. After 13 h at constant voltage, the current had decreased more than 25%.

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