

Study of membrane electrode assemblies for direct methanol fuel cells

E. Gülzow, T. Kaz, R. Reissner*, H. Sander, L. Schilling, M. v. Bradke

Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Technische Thermodynamik, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

Abstract

At DLR, membrane electrode assemblies (MEA) for direct methanol fuel cells (DMFC), are produced with the company's own dry production technique. For improving this production technique, the MEAs in fuel cells are characterized electrochemically in fuel cell test facilities as well as physically by scanning electron microscopy (SEM).

In order to measure the local current densities in polymer electrolyte membrane fuel cells, a method has been developed at DLR and tested in fuel cells supplied with hydrogen as fuel. For the DMFC, a measuring cell with 16 segments was built for examining MEAs with an overall active electrode area of 25 cm². With a sufficient resolution of location and time, simultaneous measurement of different local current densities in the cell can be carried out thus accelerating and improving operating parameter studies. This new tool is used at DLR for characterizing and developing improved MEAs and for examining the cell design (e.g. flow fields) and operating conditions of DMFC. In the measuring cell with its segments, the local mass conversion rates in the DMFC for liquid methanol–water mixtures are examined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Experimental methods; DMFC; MEA production; Characterization

1. Introduction

Direct methanol-polymer electrolyte fuel cells are being projected as potential electrochemical power sources for vehicular traction from the point of view of simplicity of design and hence, system dynamics and costs [1]. For this purpose powerful, highly efficient and low-cost fuel cell membrane electrode assemblies (MEAs) and stacks have to be developed. Usually, electrodes are prepared from a suspension of supported catalyst, PTFE and electrolyte. The suspension is applied to a carrier and then dried [2,3] before being transferred to the membrane by hot-pressing. Today, the direct methanol fuel cells (DMFC) efficiency is still not satisfactory, because the materials needed are too expensive and too high catalyst loadings are reported [4,5].

MEA development often follows a trial and error procedure. More methods of characterization apart from V–I curves are desirable to elucidate mechanisms occurring within the cell. A better understanding of those mechanisms could accelerate MEA development. There is especially a need for characterization methods that can be applied during fuel cell operation.

At DLR, a new technique for MEA production was developed that completely avoids the use of solvents and

thus necessary drying steps. Parameter variation with this technique, electrochemical and physical characterization go together on the way to solve the problems mentioned above.

2. Results and discussion

2.1. New production technique

At DLR, MEA for DMFC are produced with the company's own dry production technique. This technique was successfully introduced for preparation of MEAs for direct hydrogen PEFC [6–10]. It is now transferred to the preparation of DMFC MEAs.

The goal of development for the MEA preparation process at DLR was to achieve a low-cost and effective manufacturing process suitable for mass production. This process is based on other dry production techniques developed at DLR [11,12]. The fundamental idea of this technique is to spray a dry mixture of electrode materials either on the membrane or on the backing to avoid any waiting times for solvent evaporation. A dry coating system was developed that can handle fine powders (<0.1 μm diameter).

Fig. 1 shows the preparation steps schematically: first, a hydrophobic layer, a mixture of carbon powder and PTFE powder is sprayed onto the carbon cloth backing. Afterwards, the reaction layer is applied as a second layer consisting of supported or unsupported catalyst powders,

* Corresponding author. Tel.: +49-711-6862394;
fax: +49-711-6862747.
E-mail address: regine.reissner@dlr.de (R. Reissner).

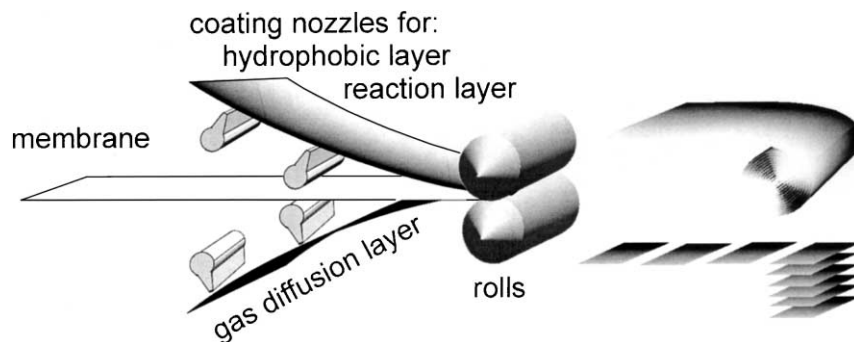


Fig. 1. Schematics of the production process for DMFC MEAs.

PTFE and possible other additives. Finally, both electrodes are fixed and bonded to the membrane by putting them through a roll heated to 160 °C. This last step can also be replaced by pressing in a heated press if a non-continuous process for MEA production is desired. It was demonstrated that reaction and hydrophobic layer thickness between 5 and 50 μm can be reproducibly produced with this technique.

Despite their different particle size and adhesion properties, this technique can handle carbon-supported as well as unsupported catalyst powders. By changing the composition of the raw powder and the deposition conditions of subsequent layers, it is possible to establish gradients, e.g. in porosity, catalyst loading or hydrophobicity in electrodes. Any, possibly hazardous, solvents are avoided. All preparation steps are simple, continuous and easily scalable thus allowing industrial MEA production. Today, a nozzle size of 50 mm is used giving electrodes of 50 mm width and length up to 1000 mm. A 100 mm nozzle has been tested with the same satisfying results. Electrodes at a width of more than 100 mm could be produced by movement of the nozzle in the y-direction.

For DMFC with liquid as well as gaseous feed of fuel MEAs were prepared with this technique. Standard materials for backing were carbon cloth (E-TEK type A), for hydrophobic layer carbon powder (Vulcan XC72) and PTFE powder (Hostafion TF 2053 by Hoechst), and for the reaction layer carbon-supported Pt, respectively PtRu (20 wt.% Pt/Vulcan XC72 by E-TEK, 20 wt.% PtRu (1:1 a/o)/Vulcan XC72 by E-TEK) and PTFE powder.

To characterize the MEA electrochemically test setups were developed that allow for automatic, continuous and safety-parameter controlled operation with liquid or gaseous methanol fuel (Fig. 2). To get information about contact and membrane resistances the cell impedance at 10 kHz is part of the standard measuring process. Measurement of the CO_2 contents in cathode exhaust gas allows to compare the methanol loss through the membrane for different MEAs.

One major difference was found between the preferred preparation technique for H_2 -PEFC and DMFC MEAs: while for PEFC it turned out to be of advantage to spray the reaction layer onto the membrane, for DMFC better MEAs were produced by spraying the reaction layer onto the

hydrophobized backing. The reason for this might be a different pore system for the different production steps. Further analysis for elucidating this observation still has to be carried out.

2.2. Physical analysis of MEAs

Apart from normal electrochemical characterization DLR MEAs as well as commercially available MEAs were also characterized by various physical methods. One question to be answered was, whether dry and ink production techniques result in the same structures and layer thickness. For this purpose, cross sections of MEAs produced with the dry DLR technique as well as those of commercial MEAs (E-TEK) were prepared by cutting and analyzed with scanning electron microscopy (SEM).

At low resolution these images could demonstrate that carbon-supported catalyst layers of the same loading resulted in layers of approximately the same thickness, especially keeping in mind that the exact composition of commercial electrodes is unknown.

With a SEM with field emission cathode, images of MEA cross sections with a high resolution and good surface sensitivity can be taken. Fig. 3 displays such high resolution images of the reaction layer of a commercial electrode and a DLR electrode. They were taken at a primary electron beam of 1 keV and secondary electrons were detected by an in-lens detector. For both images the ball-like structures are carbon (Vulcan XC72). The film-like structures as well as the net of thin fibers are due to PTFE contained in the electrode to give it the right hydrophobicity. The net of PTFE fibers also gives the electrode its mechanical stability by holding the carbon particles together. For the commercial electrode these fibers might also be due to Nafion which is not present in the reaction layers of DLR electrodes. In order to make the net of PTFE fibers visible in these images for more than one second, special measures have to be taken. At ordinary intensities of the primary electron beam PTFE fibers are quickly decomposed and evaporated. They can be stabilized by treating them at low current intensity and low voltage for several minutes. After this treatment images at normal intensities can be taken without further decomposition of the PTFE fibers.

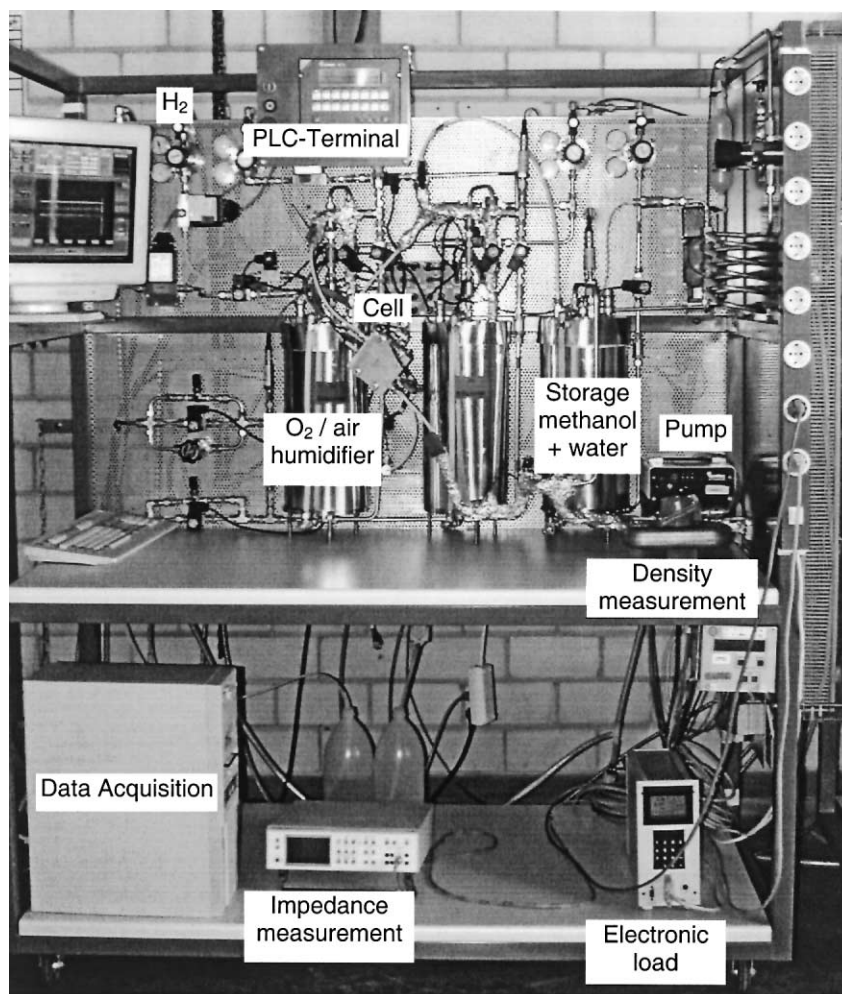


Fig. 2. Photograph of DLR test setup for lab scale I-DMFC.

It can be seen from Fig. 3 that the high resolution images for both kinds of electrodes look very much alike. Considering that the production technique for both reaction layers is quite different this is a surprising result. The commercial electrode was most likely prepared from an ink of PTFE suspension and carbon, dried and then hot-pressed to the membrane. The DLR electrode was prepared in a dry layer of carbon-PTFE powder mixture and then hot-pressed to the membrane, as described above. Obviously, these two techniques result in the same physical structures.

2.3. Current density distribution across the cell

Usually, V–I curves are registered assuming that there are no major inhomogeneities across small laboratory cells. In order to see if this assumption is correct a cell was constructed at DLR that allows us to measure current density distributions in a 25 cm² laboratory cell without interfering with the cell operation. Fig. 4 displays the design of this cell. The normal cell frame is divided into 16 segments with a side length of 12.5 mm insulated towards each other. The

current that is generated in this region of the cell flows through a small series resistance. The entire cell current flows through a copper current collector behind these series resistances and can be controlled the same way as for operating a non-segmented cell. The voltage drop along the 16 resistances is scanned and the resulting current density distribution across the cell is registered as well as displayed on-line on a computer. With the apparatus presently used it takes 20 s for one current density distribution image but faster apparatus is on the way. The flow field presently used in this cell is a chocolate water structure. While the segmented measuring cell is used as current collector and flow field for one electrode, the other electrode is not segmented and can have any flow field design. Further technical details on this cell will be reported in a forthcoming paper [13].

This cell has been used in hydrogen fuel cell as well as for DMFC measurements. In all cases it was found that the assumption of mostly constant conditions across a 25 cm² laboratory cell is almost never realized. It could be demonstrated that especially the water management, poisoning

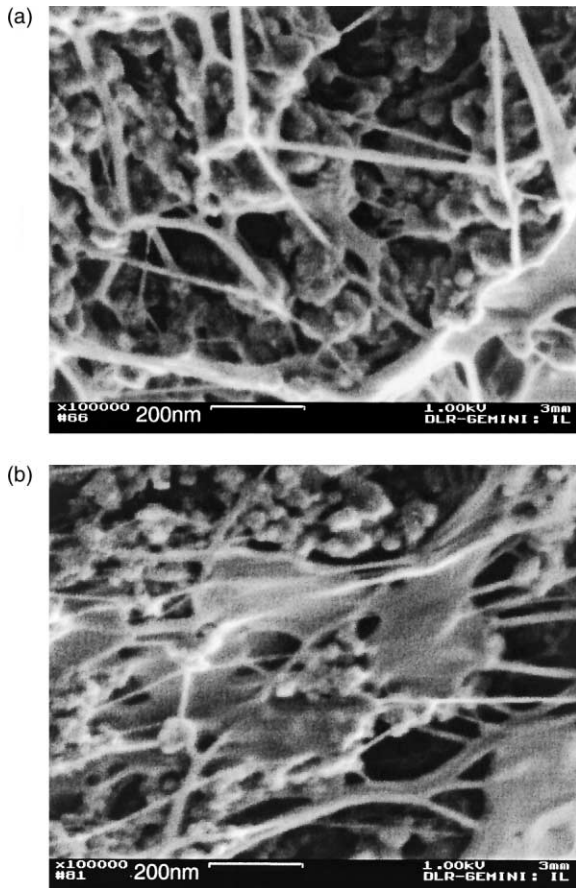


Fig. 3. High resolution SEM images of cross section of reaction layer. (a) Commercial electrode with 1 mg/cm^2 30 wt.% PtRu (1:1 a/o)/Vulcan XC72, Nafion impregnation; (b) DLR electrode with 0.5 mg/cm^2 PtRu (1:1 a/o)/Vulcan XC72, layer containing 20 wt.% PTFE.

effects, inhomogeneous mounting of the cell, MEA inhomogeneity and flow field influence are not only relevant in a cell of technical size [14] but also in a small laboratory cell.

As a first result obtained with this cell, Figs. 5 and 6 display an investigation of different DMFC cathode flow fields. In both cases the measuring cell was the anode. In an independent measurement without MEA the flow lines of the methanol water mixture across this flow field were investigated. To do so the single flow fields were covered with an acrylic glass plate and the liquid and gas flows used in the fuel cell experiment were run through the flow structure. To make the flow lines visible a small amount of water was added to the gas flow and a small amount of gas to the liquid flow. It could be demonstrated that the liquid flow did not reach all the corners in the cell, as shown in Fig. 5. For the cathode a chocolate water structure was used in one experiment, a meander structure in another experiment. MEA and operating conditions (e.g. air flux) were the same in both experiments. As can be seen in Fig. 6 the current density distribution across a cell with the meander cathode is a lot more homogeneous than for the chocolate water cathode. For the meander, a reduced activity in the

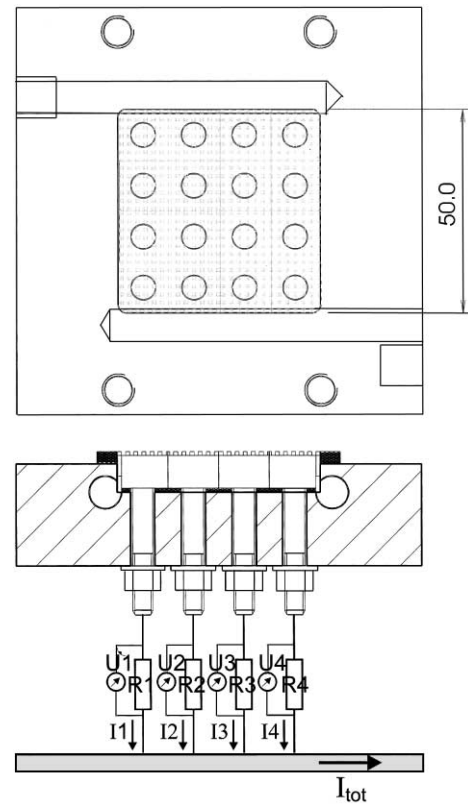


Fig. 4. Schematic drawing of the construction and operating principle for the segmented cell for current density distribution measurements.

region where the dry gas enters the cell might be due to a reduced humidity of the membrane in this region. Within the cell the cathode flow takes up a lot of liquid water. Thus, towards the exit of the cell an increased flooding of the cathode leads to a slightly reduced activity. For the chocolate water cathode, the current density distribution looks quite different. Even though the independent flow structure measurement displayed a homogeneous flow cross the cathode, conditions during operation of the fuel cell seem to be quite different. High activity is only observed in the center of the cell whereas the corners are almost inactive. Extremely low activities at the bottom of the cell could be due to flooding of the cathode close to the cell exit and to a liquid water accumulation at the bottom due to gravity. Unlike the meander structure, the air is not forced to supply every part of the cell possibly resulting in regions that remain flooded all the time. A good explanation for the observed current density distribution could not yet be found. The overall cell current for the meander cathode structure is higher not only due to the more equal current density distribution but also to the higher air flux in the meander channels. A drawback of this higher flux is an increased pressure drop across the cell that would become especially serious for cells at technical size.

Further DMFC measurements will be reported in a forthcoming paper.

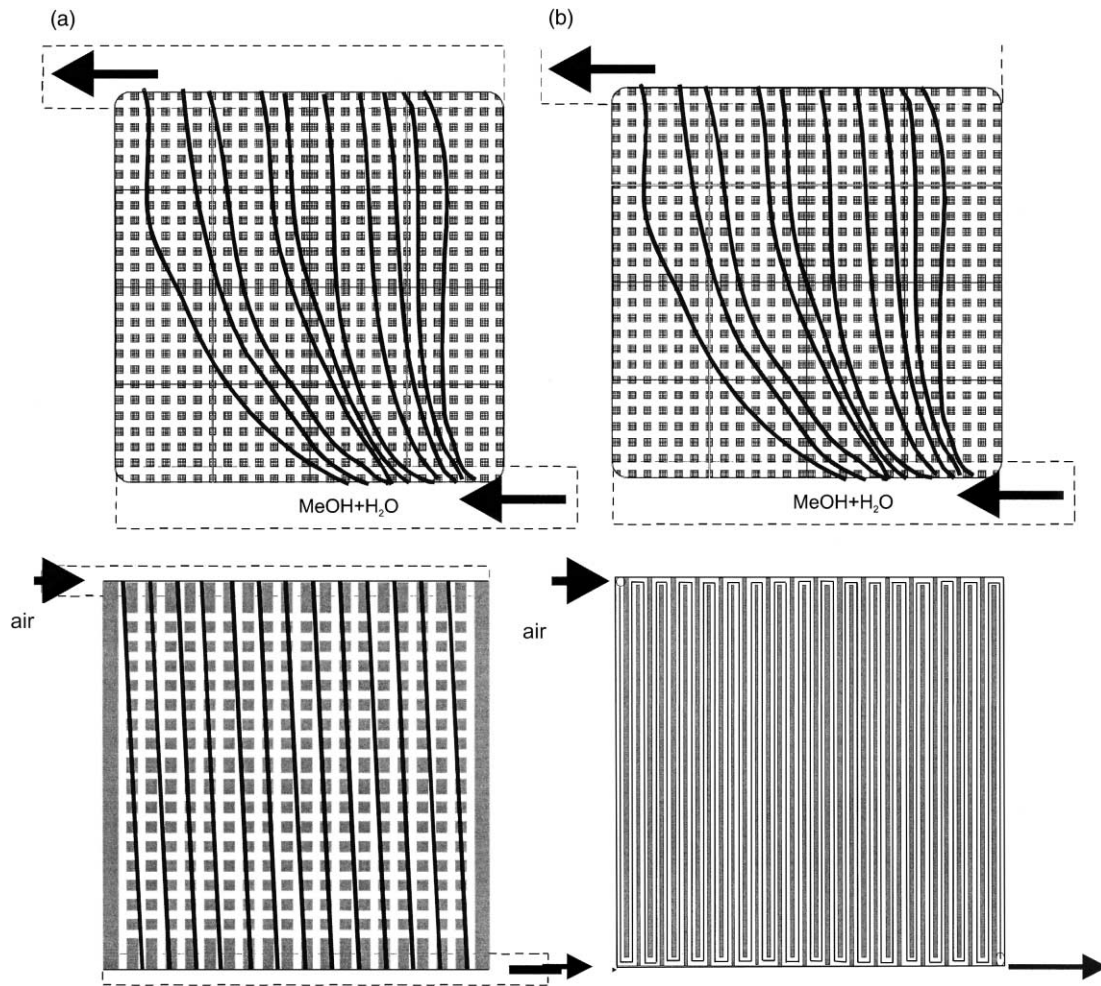


Fig. 5. Orientation and size of flow fields with respect to measuring results in Fig. 6. For both measurements (a) and (b), the segmented cell with its chocolate water structure flow field was used as anode. The cathode flow field for (a) was a chocolate water structure, for (b) a single meander structure. Indicated by lines are the flow patterns of water + methanol at the anode and air at the cathode investigated at the fluxes used in the DMFC experiment. These flow patterns were observed without DMFC operation and at room temperature.

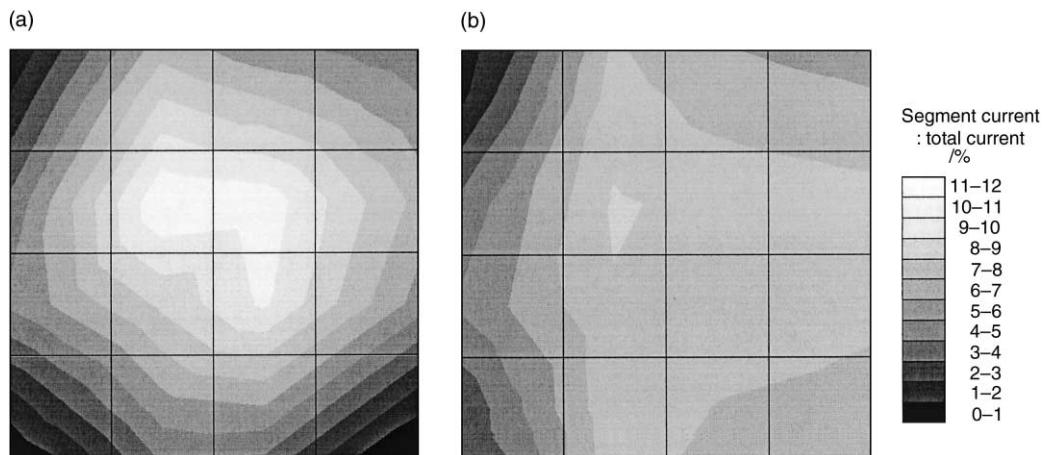


Fig. 6. Current density distribution for different cathode flow fields: (a) cathode chocolate water structure, (b) cathode meander flow field. Measured relative current densities for each segment (in % of total cell current) are displayed in the middle of each segment, other values are interpolated and extrapolated. MEA: anode E-TEK ELAT 1 mg/cm² 30 wt.% PtRu (1:1 a/o)/C, impregnated with 40 μl/cm² Nafion solution (Aldrich); cathode E-TEK ELAT 0.4 mg/cm² Pt/C with 0.7 mg/cm² Nafion; membrane Nafion 117; MEA pressed at 160 °C, 2 min. Operating conditions: anode 20 ml/min, 1.5 M methanol solution, 2.5 bar_{abs}; cathode 600 ml/min dry air, 3 bar_{abs}; 90 °C. The average current density for the cell was (a) 238 mA/cm² at 200 mV, (b) 321 mA/cm² at 200 mV.

3. Conclusions

A low-cost production technique [7] for MEAs was developed that allows us to prepare MEAs for PEFC and DMFC. Different catalyst materials can be handled and a large number of preparation parameters allows us to adapt MEA properties for different needs. While today these H₂-PEFC MEAs display V–I curves comparable to others published in the literature or measured at our lab with commercially available electrodes, the development of DMFC still goes on. This development is supported by characterization of MEAs with various physical and electrochemical methods. No difference in electrode structure of these MEAs compared to other production techniques could be observed.

Current densities across the cell were measured with a newly developed tool without interfering with the fuel cell operation. This technique allows dynamic, on-line displayable measurements. As a first result the strong difference in current density distribution for different cathode flow fields was presented.

Acknowledgements

Support by the Baden-Württemberg Ministry of Science, Research and the Arts and the Stiftung Energieforschung Baden-Württemberg is gratefully acknowledged.

References

- [1] K. Kordesch, G. Simader, Fuel Cells and their Applications, VCH, Weinheim, 1996.
- [2] M. Uchida, Y. Fukoua, S. Sugawara, E. Eda, J. Electrochem. Soc. 143 (1996) 224445.
- [3] S. Gottesfeld, T.A. Zawodzinski, Polymer electrolyte fuel cells, in: R.C. Alkire, H. Gerischer, D.M. Kolb, Ch.W. Tobias (Eds.), Advances in Electrochemical Science and Engineering, Vol. 5, Wiley-VCH, Weinheim, 1997, p. 229.
- [4] M. Baldauf, W. Preidel, J. Power Sources 84 (1999) 161.
- [5] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 111.
- [6] E. Gülzow, M. Schulze, N. Wagner, T. Kaz, R. Reissner, G. Steinhilber, A. Schneider, J. Power Sources 86 (2000) 352.
- [7] E. Gülzow, M. Schulze, N. Wagner, T. Kaz, A. Schneider, R. Reissner, Fuel Cell Bull. 15 (1999) 8.
- [8] D. Bevers, N. Wagner, Verfahren zur Herstellung eines Verbundes aus Elektrodenmaterial, Katalysatormaterial und einer Festelektrolytmembran, Patentschrift DE 19509749 C2.
- [9] D. Bevers, N. Wagner, Patent no. DE 19509749 C2, 1997.
- [10] A. Helmbold, Verfahren zur Herstellung von Funktionsschichten für Brennstoffzellen, Deutsches, Patent no. DE 19757492 A1, 1999.
- [11] D. Bevers, N. Wagner, M. von Bradke, Int. J. Hydrogen Energy 23 (1997) 57.
- [12] D. Bevers, N. Wagner, M. von Bradke, J. Hydrogen Power 63 (1996) 193.
- [13] H. Sander et al, in preparation.
- [14] C. Wieser, A. Helmbold, E. Gülzow, J. Appl. Electrochem. 30 (2000) 803.