Manufacturing Technologies for Direct Methanol Fuel Cells (DMFCs)

A. Glüsen, M. Müller, N. Kimiaie, I. Konradi, J. Mergel, D. Stolten

This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 1: Fuel Cell Basics / Fuel Infrastructures
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-1
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-651-4

Manufacturing Technologies for Direct Methanol Fuel Cells (DMFCs)

Andreas Glüsen, **Martin Müller**, **Nicola Kimiaie**, **Irene Konradi**, **Jürgen Mergel**, **Detlef Stolten**, Institute of Energy Research – IEF-3: Fuel Cells, Forschungszentrum Jülich, Germany

1 Introduction

Fuel cell research is focussing on increasing power density and lifetime and reducing costs of the whole fuel cell system [1]. In order to reach these aims, it is necessary to develop appropriately designed components outgoing from high quality materials, a suitable manufacturing process and a well balanced system.

To make use of the advantages that can be obtained by developing production technology, we are mainly improving the coating and assembling techniques for polymer electrolyte fuel cells, especially Direct Methanol Fuel Cells (DMFCs). Coating is used for making fuel cell electrodes as well as highly conductive contacts. Assembling is used to join larger components like membrane electrode assemblies (MEAs) and bipolar units consisting of flow fields and the separator plate, as well as entire stacks.

On the one hand a reproducible manufacturing process is required to study fine differences in fuel cell performance affected by new materials or new designs. On the other hand a change in each parameter of the manufacturing process itself can change product properties and therefore affect fuel cell performance.

As a result, gas diffusion electrodes (GDEs) are now produced automatically in square-meter batches, the hot-pressing of MEAs is a fully automated process and by pre-assembling the number of parts that have to be assembled in a stack was reduced by a factor of 10. These achievements make DMFC manufacturing more reproducible and less error-prone. All these and further developments of manufacturing technology are necessary to make DMFCs ready for the market.

2 Coating Technology

An important manufacturing step for Direct Methanol Fuel Cells is the preparation of fuel cell electrodes by coating techniques. It is our aim to understand and, in a later step, to take advantage of the influence of coating technology on electrode properties. For our new pilot production facility, built in 2008/2009 (see below), we chose complementary coating techniques in order to allow comparing different techniques for electrode preparation as well as different ways to integrate the catalyst layer into the membrane electrode assembly (MEA). The electrodes can be prepared onto a gas diffusion layer (GDL) to form a gas diffusion electrode (GDE) or onto a membrane to form a catalyst coated membrane (CCM) [2]. A catalyst layer can be made in one coating step or by coating several thin layers on top of each other. The coating techniques available in Jülich are knife-coating, slot-coating and screen-printing.

2.1 GDE-manufacture by knife-coating

In the past 8 years manual small-scale manufacturing of GDEs was transferred in Jülich to a continuous roll-to-roll knife coating process. GDLs and GDEs are now routinely manufactured in widths of up to 45 cm and a maximum continuous length of 45 meters. For the manufacture of a 90-cell DMFC stack in the kW-class for use in a horizontal order picker in 2009, 30 meters of GDL were continuously manufactured and used as the substrate for the manufacture of GDEs in 5 batches. Batch-size for GDEs was limited because of the high cost of noble metal catalyst and the resulting high economic risk in case of an (improbable) failure of a coating batch. GDL manufacture was made by coating a layer consisting of PTFE (40%) and carbon black (60%) onto teflonized carbon fabric. Dry coating weight was 3.7 mg/cm² with a standard deviation of 0.3 mg/cm² as determined from 80 samples of 20 cm² taken at various positions along the length and the width of the GDL. The standard deviation was approximately the same when comparing samples taken at one lateral position along the length of the GDL and for samples taken at one longitudinal position across the GDL. On top of this GDL the catalyst layers were coated with an average noble metal loading of 2.2 mg/cm² (cathodes) and 2.3 mg/cm² (anodes) and a standard deviation of 0.1 mg/cm² in both cases. Due to this good reproducibility the performance of the individual cells in a 90-cell DMFC stack is very homogeneous as can be seen in Figure 1. Lower cell voltages in the first and the last cell are probably due to thermal loss through the end-plates.

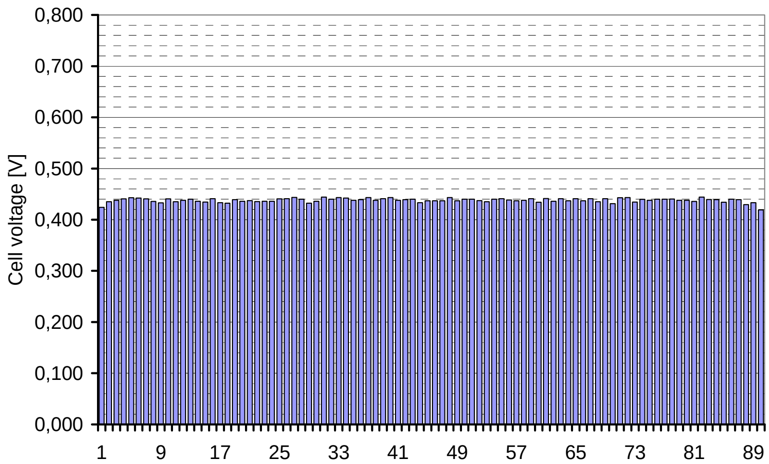

Figure 1: Cell voltage distribution in a 90 cell DMFC stack at a current density of 0.16 A/cm², 70 °C and high air flow rates.

2.2 Advanced coating equipment

In order to further optimize coating technology, a new coating facility was set up in Jülich in 2008 and 2009. In the new coating facility equipment for knife coating, for slot coating and for screen-printing is available. A flexible roll-to-roll coating machine is available for knife coating and slot coating. It has been constructed by Coatema under the brand-name Click & Coat [3]. It consists of several individual modules, which can be combined to a coating machine as required for a specific coating task. Figure 2 shows a coating machine made by combining several different modules. Figure 3 shows schematically how the machine can be modified to compare different manufacturing processes. While the final production process for GDEs will contain coating and several processing steps, for example drying, sintering and calendering, it may be useful to find out, how the individual process steps can best be combined. For example, it can be studied by changing the machine setup if calendering is more effective before or after sintering. A simpler machine can be combined to just study the basic process consisting of coating and drying. The resulting raw electrode can then be fed into another setup to study and optimize one individual process step. Another roll-to-roll coating machine is specifically designed for slot-coating both sides of a membrane at the same time. This will allow continuous manufacture of CCMs. Single-sided slot-coating is also possible with this machine and will be used for coating membranes as well as decal substrates. Screen printing is done with a standard screen printer as routinely used in the electronics industry.

Figure 2: Flexible coating machine made up of several modules.

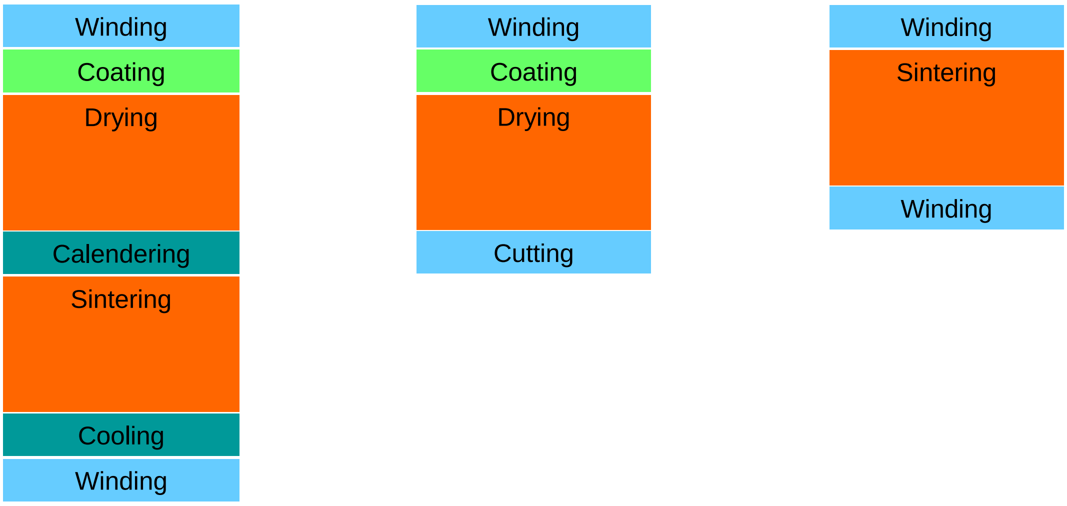

Figure 3: Schematic representation of different machine setups; left: complex machine for coating and several post-processing steps, middle: simple coating machine, right: machine for studying one processing step (here: sintering).

2.3 Substrate for electrode preparation

When electrodes are made by coating onto a GDL (GDE-route), coating is usually easy because the substrate is mechanically and dimensionally relatively stable. All coating techniques are suitable for this route and it is therefore this route that is currently used for all large scale manufacturing projects in Jülich. Coating onto membrane is more difficult, because many membranes are not as stable as the GDLs and because membranes tend to swell during the coating process due to the solvent used in the catalyst ink. These problems can best be avoided by using the screen-printing technique. During the printing process the screen is pressed onto the substrate by the squeegee. This results in a flat substrate during coating even if swelling occurs. An alternative is to coat and dry the catalyst layer on a so called decal substrate and transfer the catalyst layer to the membrane by hot-pressing.

2.4 Coating techniques

Different coating techniques can be used to make catalyst layers from a catalyst ink and they all have their specific advantages and disadvantages. Therefore it is necessary to compare different coating techniques in order to use the best technique for each coating application. The techniques differ in the geometries that can be coated and in the influence the substrate has on the coating result. A general differentiation is between a continuous process where the substrate is passed from roll to roll through the coating equipment and a discontinuous process where individual sheets of substrate are coated one after the other.

Knife coating and slot coating are continuous processes whereas screen-printing is a discontinuous process. The amount of catalyst ink applied in the knife coating process is controlled by the distance of the coating knife and the substrate. The porosity of the substrate, however, leads to an additional amount of ink that penetrates into the substrate. In the slot coating process in contrast, the amount of catalyst applied to the substrate is controlled by a metering pump and independent of the substrate. In both cases the coating amount can be varied continuously. The screen used for screen-printing determines the amount of catalyst ink applied to the substrate. For each variation of the amount of catalyst ink, a different screen has to be made.

3 Assembling

The fabrication of fuel cells and their components can be broken down into a number of assembly steps. The monitoring and verification of material flows and the associated documentation are crucial processes in all assembly steps. The DMFC stacks in the kW range developed at IEF-3 have an active cell area of 315 cm² and mainly consist of graphite bipolar plates. For stacks with lower power output stainless steel or other alloys were also tested. In this article the focus is on the assembling process of the graphite material. The assembling of these stacks is consisting of different production steps:

- Manufacturing of the structures by punch cutting and laser or water beam cutting
- Pre-assembly of membrane electrode assemblies (MEAs)
- Pre-assembly of bipolar units outside the stack
- Robot assisted stacking of bipolar units and MEAs

- Mechanical fastening of the stack
- Installation of faceplates

3.1 Membrane electrode assemblies

Outgoing from coated substrates the membrane electrode assemblies (MEAs) were built up. This is done under a temperature of 130 °C and a defined pressure [4] in a hot pressing module. The process is fully automated so that reproducibility can be guaranteed. Figure 4 shows on the left hand the subcomponents of the MEA: Membrane, anodic and cathodic GDE and stabilizing frames. On the right hand the robot assisted supply of the MEA components into the hot pressing module is shown, next to the hot pressing module is a further press module for cooling the components from 130 °C down to environmental temperature. During the pressing process the parameters temperature, pressure and distance between the hardboards are electronically logged.

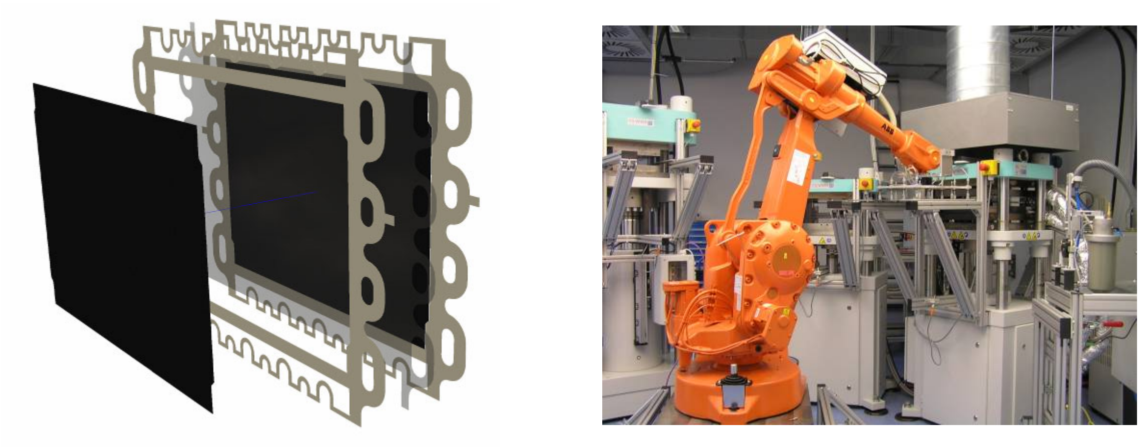

Figure 4: MEA setup and robot assisted MEA production.

The challenge is in handling the flexible electrodes and the flexible membrane under moisture expansion. During this assembling step the very flexible structures of the membrane and the electrodes are transformed in the frame stabilized MEA structure that is easy to handle. After the assembling process the MEAs are ready for stack integration and electrochemical tests.

3.2 Pre-assembly of bipolar units

To produce stacks with a homogeneous media distribution and an even cell voltage distribution it is necessary that the manufacturing tolerances are not affected by the assembly process itself. This is difficult especially if flexible materials like expanded graphite are used. The bipolar units used in DMFC stacks developed at IEF-3 consist among other things of three different expanded graphite layers. By building up the bipolar unit in layers it is possible to adapt the material properties better to the functional demands of each layer. The bipolar unit consists of the flexible cathodic flow field, the firm separator plate, the flexible anodic flow field, centering bolts and a very flexible wick (Figure 5).

One way to achieve a precise and reproducible bipolar unit is to fix these subcomponents with adhesives in a pre-assembling process. With a special adhesive that is stable under the anodic and cathodic conditions and which releases no ionic or organic impurities the different parts of the bipolar unit get bonded.

Pre-assembling of the bipolar unit reduces the number of parts by a factor of eight during the stack assembling process. Compared with using three flexible layers the assembly of the bipolar unit allows to control the manufacturing tolerances before the stack assembly.

The pre-assembling of the bipolar unit is done automatically by a robot technology. The adhesive is deposited on the components by a robot based sprayer. After the deposition of the adhesive the components of the bipolar unit are stacked by the robot (Figure 5). Finally the parts get bonded under pressure and temperature inside the hot pressing module.

The repeat accuracy of the robot is 0.06 mm. Compared with a manual assembly this is very accurate. Furthermore the robot system is flexible so that different tools like vacuum gripper, dispenser and sprayer can be used. A quick release tooling system allows different tools to be connected to the robot with a change-over time of only a few seconds, whereby the robot grips the required tool itself.

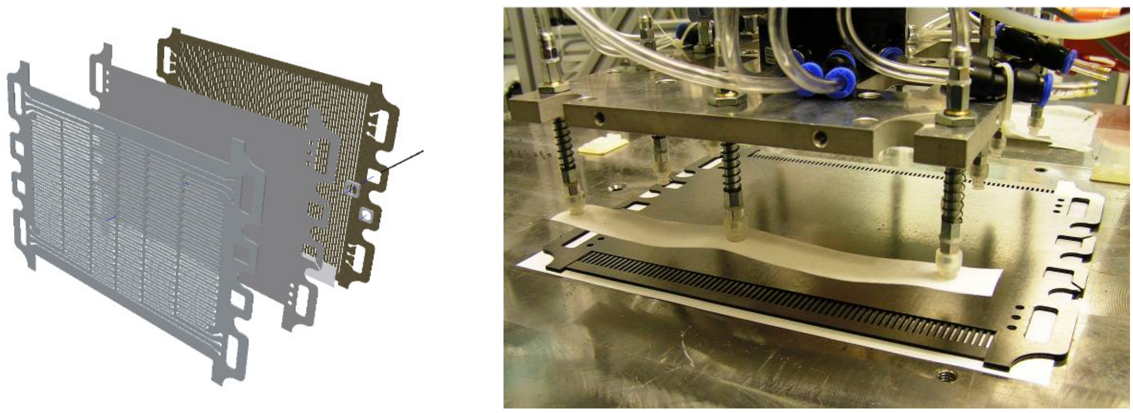

Figure 5: Bipolar unit setup and robot assisted assembly of wick.

3.3 Quality assurance

To know if a different cell performance is affected by a new design or different manufacturing techniques it is necessary to control the manufacturing tolerances of each component of the stack. It is essential that the dimensional compliance is verified in order to reveal possible errors as early as possible.

In contrast to standard components, which have a limited number of characteristic dimensions, a topographic profile of large surfaces must be created for fuel cells. This can be done with the aid of a non-contact 3D laser measurement system and the corresponding analysis software (see Figure 6). Measurement accuracies up to 0.01 µm can be achieved.

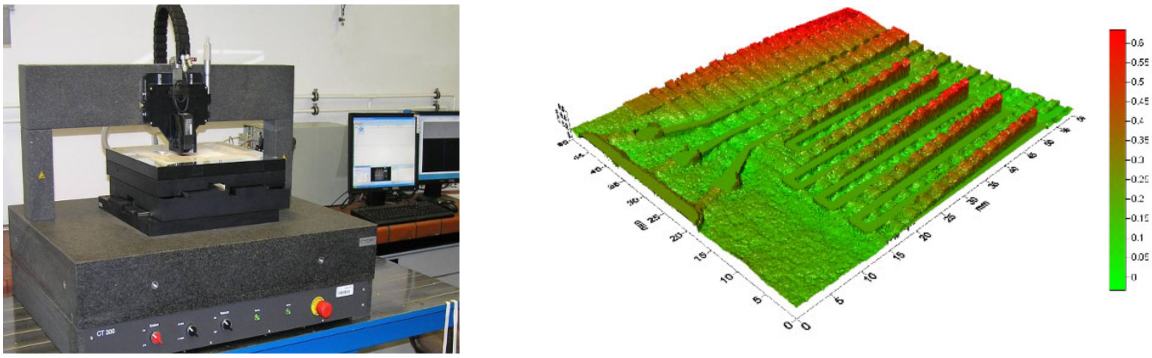

Figure 6: Laser scan device and results of bipolar unit scanning.

3.4 Stack assembling

After all components have passed preassembling and quality control the stack can be built up. Figure 7 shows on the left hand a 90-cell stack built up in 2009 and on the right hand a polarization plot of the same stack at an operating temperature of 70 °C and a methanol concentration in the anodic loop of one mole per litre. This stack is a result of a government-funded project with the aim of introducing DMFC technology into horizontal order pickers. After the first electrochemical tests the stack was integrated into a DMFC system that fits into a horizontal order picker for a 3,000 h duration test [5].

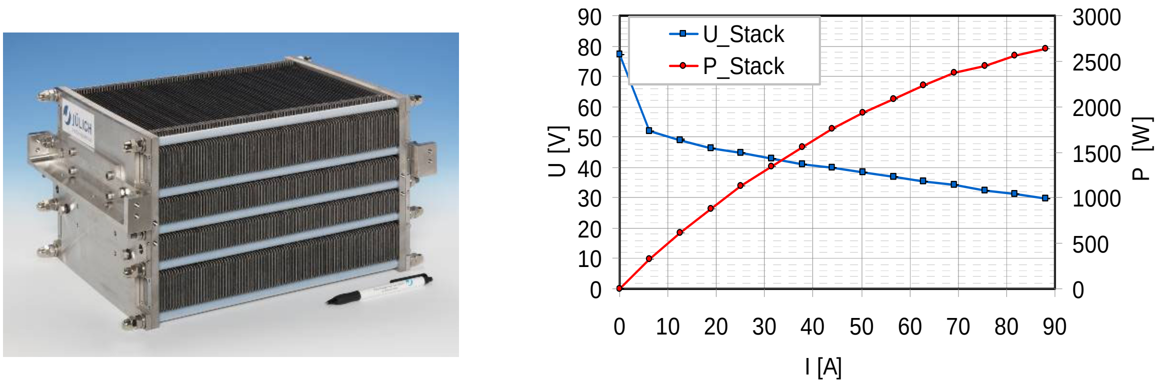

Figure 7: 90-cell DMFC stack and polarization plot.

References

[1] J. Mergel, A. Glüsen, C. Wannek: „Current Status of and Recent Developments in Direct Liquid Fuel Cells“ p. 41ff in D. Stolten (ed.) “Hydrogen and Fuel Cells” Wiley VCH, Weinheim 2010

[2] Q. Mao, G. Q. Sun, S. L. Wang, H. Sun, G. X. Wang, Y. Gao, A. W. Ye, Y. Tian, Q. Xin: „Comparative studies of configurations and preparation methods for direct methanol fuel cell electrodes”, *Electrochimica Acta* 52, 6763 (2007)

[3] T. Kolbusch, A. Glüsen, J. Mergel: „Manufacturing Processes for Gas-Diffusion Electrodes for Polymer Electrolyte Fuel Cells", Presented at World Hydrogen Energy Conference WHEC 2010 Essen: 16.05.2010 – 21.05.2010 and Chapter in this book

[4] A. S. Aricò, P. Cretì, P. L. Antonucci, J. Cho, H. Kim, V. Antonucci: "Optimization of operating parameters of a direct methanol fuel cell and physico-chemical investigation of catalyst-electrolyte interface" *Electrochimica Acta* 43, 3719 (1998)

[5] H. Jansen, M. Hehemann, J. Mergel, D. Stolten: „System technology aspects for light traction applications of direct methanol fuel cells", Presented at World Hydrogen Energy Conference WHEC 2010 Essen: 16.05.2010 – 21.05.2010 and Chapter in this book