

New results of PEFC electrodes produced by the DLR dry preparation technique

Erich Gülzow^{*}, Till Kaz

Institut für Technische Thermodynamik DLR Stuttgart, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

Abstract

At DLR Stuttgart a dry production technique has been developed for the preparation of electrodes and membrane electrode assemblies (MEA) for hydrogen PEFC as well as for direct methanol PEFC. Different spray strategies and different mixtures of electrodes and catalysts were tested to improve cell performance and reproducibility. The main advantage of the dry production technique [J. Power Sources 86 (2000) 352, Fuel Cell Bull. 15 (1999) 8] is the solvent-free coating of the electrodes, which allows a continuous production of MEA. In addition, thin layers (<5 μm) can be produced saving expensive catalyst material. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

DLR has designed a dry production technique for membrane electrode assemblies (MEA) [1,2] which causes low costs and is also environmentally friendly. In this paper, the improvement of the MEA performance based on changes in the production parameters and materials is described. All the materials used for the preparation of MEA, catalysts, polymers, membranes and gas-diffusion-layers (GDL) are commercially available.

2. Experimental

The MEA were tested in single cells, both end plates for the anode as well as for the cathode were designed with a single meander structure for the gas supply of the electrodes. The test cells were integrated in fully automatic test facilities operating with programmed logic controller (PLC) for security management and data acquisition [3]. The start-up procedure was performed with humidified gases under potential control. The MEA were electrochemically characterised at 80 °C with pure hydrogen and with pure oxygen or air by having $V-i$ characteristics recorded. The MEA were typically characterised with hydrogen and oxygen or air at a pressure of 2 bar.

3. Results

3.1. MEA with supported catalysts

When the development of the dry spraying production technique for PEFC, MEA was started, the catalyst (Vulcan XC-72 20% platinum (E-Tek)) was mixed with 20% PTFE (Hoechst) and the powder was sprayed on the GDL, later on the electrodes were pressed with a Nafion[®] 117 membrane. As the electrochemical performance of MEA identically prepared with this procedure differed by over 20%, the reproducibility of these MEA was not satisfactory. Thus, in the next step of the development the spraying strategy was changed from spraying the electrode powder onto the GDL to spraying the powder directly onto the membrane. The electrochemical performance of the electrodes became more reproducible and the variance was decreased to approximately 5%, while the electrochemical performance was improved, too. Fig. 1 shows the $V-i$ characteristic of three MEA with electrodes sprayed directly onto the membrane. By coating the membrane with the powder the connection between both of these parts was improved and consequently the electrochemical performance as well. The surface of the membrane is then very flat compared with the surface of the GDL. Therefore, the coated layer is more homogeneous on the membrane than on the GDL and the powder sprayed on the membrane is totally incorporated in the reaction layer. In contrast, a part of the powder sprayed in the GDL penetrates the GDL so that there is no powder in the reaction layer.

^{*} Corresponding author. Fax: +49-711-6862-747.
E-mail address: erich.gulzow@dlr.de (E. Gülzow).

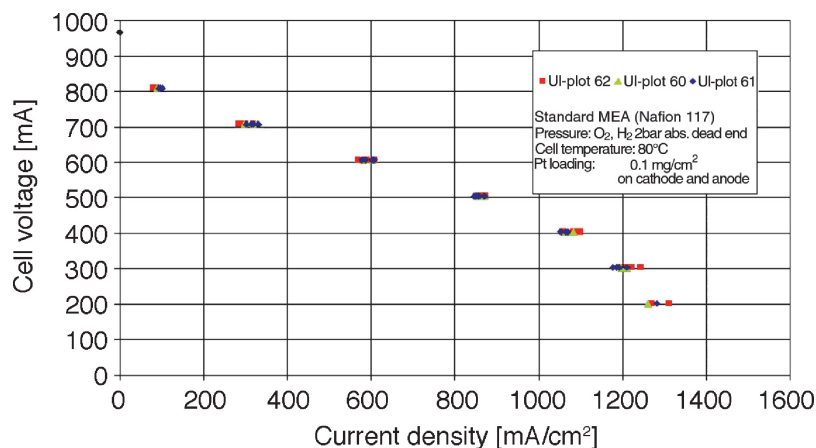


Fig. 1. Reproducibility of three MEA with Nafion[®] 117 membranes.

As a consequence of the roughness of the GDL surface the electrode preparation is not so much reproducible when the powder is sprayed onto the GDL, while spraying onto the flat membrane surface allows a reproducible preparation of the reaction layers.

To investigate the influence of the membrane thickness on the cell performance MEAs with two different kinds of membranes (Nafion[®] 117 (175 μm) and Nafion[®] 112 (50 μm)) were prepared and characterised. With the Nafion[®] 112 membrane the cell performance at 500 mV could be improved by 200 mA/cm^2 compared to the Nafion[®] 117 membrane. By using the Nafion[®] 112 membrane the electrochemical performance is improved by two effects: due to the lower thickness the membrane resistance is decreased. In addition, the water balance is more uncritical when using a thin membrane than it is with the thick Nafion[®] 117 membrane, which effects the transport processes in the electrodes positive [4].

Simultaneously, the difference between hot-pressing and rolling of the MEA was investigated. For a continuous production technique a rolling process instead of a batch process like hot-pressing would be preferable. Fig. 2 shows

the $V-i$ characteristics of a pressed and a rolled MEA with Nafion[®] 112 membranes. As there were some difficulties with the handling of the Nafion[®] 112 membrane, a Nafion[®] 1135 (80 μm) membrane was chosen.

There are only few possibilities where the operation of fuel cells with pure oxygen can be used in closed systems, e.g. in applications for space missions or submarines. To be able to compare the DLR MEA with other MEA the conditions of the characterisation were changed from using pure oxygen to using air on the cathode as well. Fig. 3 shows the comparison of an MEA with a Nafion[®] 1135 membrane tested with oxygen and with air. A loss of nearly 50% in the cell performance is visible when using air on the cathode.

To increase the active surface of the electrode, MEA with different mixtures of 20% supported catalyst and Nafion[®] powder were prepared. The Nafion[®] powder was manufactured by grinding Nafion[®] pellets in a ball mill cooled with liquid nitrogen (diameter of the Nafion[®] - powder: 5–10 μm) [5]. An improvement of the cell output could not be achieved, it seemed that there was no ionic contact between the catalyst and the electrolyte due to the big difference of the size of active platinum clusters, the catalyst supporting

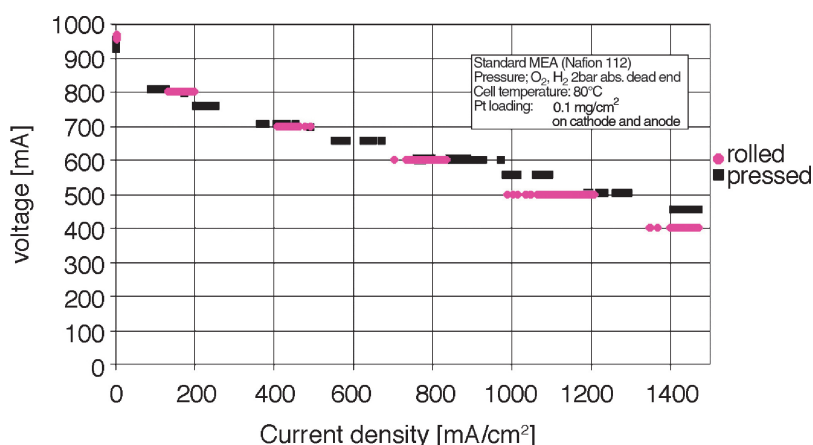


Fig. 2. Comparison of pressed and rolled MEA with Nafion[®] 112 membranes.

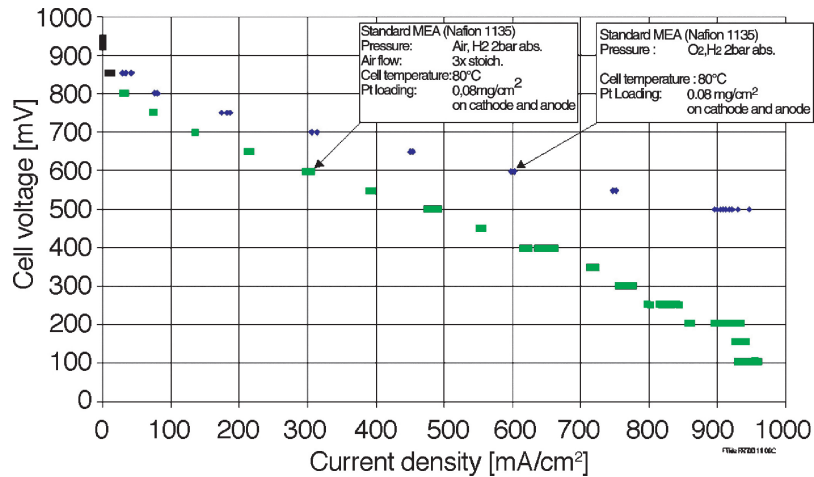


Fig. 3. Test of an MEA with oxygen and with air on the cathode.

carbon and Nafion[®] particles. The carbon surface is not active for the reaction as well as it may not support the transport of the intermediates like protons formed on the catalyst surface. The problem of the poor ionic contact between catalyst and electrolyte may be solved by using higher loading of platinum on the carbon, because a higher rate of the supporting carbon is covered by the active platinum clusters.

3.2. MEA with unsupported catalysts

A study at the Paul Scherrer Institute [6] showed that the platinum surface has a high proton conductivity. In order to avoid any ionic isolator, the supported catalyst was replaced by an unsupported one. It was no problem to adapt the coating device to unsupported catalysts as the size of the unsupported and supported catalysts is nearly the same (30 nm) [7].

In the first experiment we prepared MEA with a mixture of 70% unsupported catalyst (platinum black (E-Tek)) and 30% Nafion[®] powder in the electrode. The loading for the

whole MEA was 1.0 mg Pt/cm² (0.5 mg/cm² on each electrode). An electrochemical impedance study showed that the electrochemical performance with identical electrodes on the anode and the cathodes is clearly dominated by the cathode kinetics, the losses on the anode were significantly lower [8]. Therefore, a decrease of the anode performance may hardly influence the MEA performance, so the platinum loading on the anode can be reduced. The anode was coated with a mixture of supported catalyst and PTFE. The MEA had a platinum loading of 0.1 mg Pt/cm² on the anode and 0.5 mg Pt/cm² on the cathode. Fig. 4 shows the *V*–*i* curve of the MEA with supported and unsupported catalyst on the anode. The performance of these MEA is nearly the same.

For the future development the following points still have to be investigated:

- Where is the optimum ratio of Nafion[®] and unsupported catalyst?
- Is Nafion[®] really necessary for the proton transport when using unsupported catalyst?

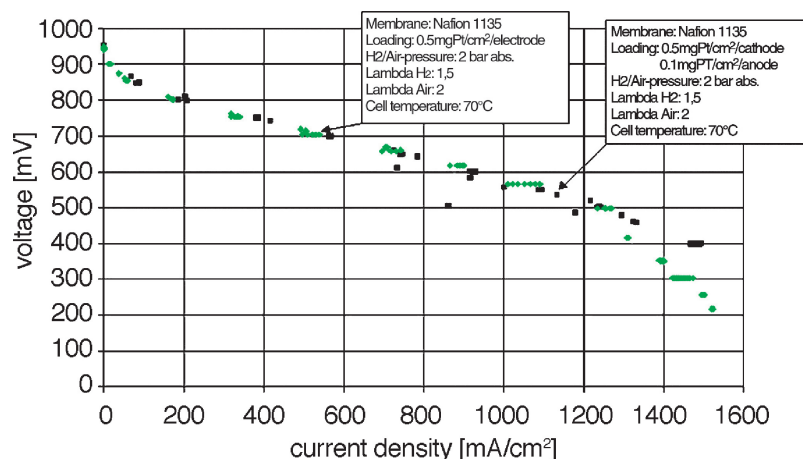


Fig. 4. Comparison of supported and unsupported catalyst on the anode.

- Which platinum loading of a carbon supported catalyst is necessary to connect the total platinum surface with ionic conductivity paths with Nafion[®]?
- Is the function of Nafion[®] in the electrode limited to the proton transport or is Nafion[®] also involved in the regulation of the water balance?
- Does Nafion[®] effect the long-term stability?

4. Conclusion

The dry production technique of MEA has several advantages compared with wet coating techniques. It is an uncomplicated process and has a high degree of automation. Furthermore, it is a scientific tool to develop MEA systematically concerning the electrode composition, which is necessary to understand the properties of the individual components and the correlation to the properties of components in combination. The dry spraying technique can easily be adapted to new materials and material combinations and therefore new materials can easily be characterised in

prepared MEA. A minimum of material is used for the MEA production.

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