Effects of membrane electrode assembly preparation on the polymer electrolyte membrane fuel cell performance

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Abstract

This paper presents results of recent investigations to develop an optimized in-house membrane electrode assembly (MEA) preparation technique combining catalyst ink spraying and assembly hot pressing. Only easy steps were chosen in this preparation technique in order to simplify the method, aiming at cost reduction. The influence of MEA fabrication parameters like electrode pressing or annealing on the performance of hydrogen fuel cells was studied by single cell measurements with H_2/O_2 operation. Toray paper and carbon cloth as gas diffusion layer (GDL) materials were compared and the composition of electrode inks was optimized with regard to most favorable fuel cell performance. Commercial E-TEK catalyst was used on the anode and cathode with Pt loadings of 0.4 and 0.6 mg/cm², respectively. The MEA with best performance delivered approximately 0.58 W/cm², at 65 °C cell temperature, 80 °C anode humidification, dry cathode and ambient pressure on both electrodes. The results show, that changing electrode compositions or the use of different materials with same functionality (e.g. different GDLs), have a larger effect on fuel cell performance than changing preparation parameters like hot pressing or spraying conditions, studied in previous work.
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1. Introduction

The advantages of fuel cells as energy converters are well known. They produce electricity and heat by electrochemical reactions directly from chemical energy. Fuel cells have only low (or no) emissions and operate with high efficiency. Due to their high flexibility, fuel cells are a favored option for a variety of applications like vehicle propulsion and stationary or portable power supply [1–4]. Polymer electrolyte membrane fuel cells (PEMFC) have probably the largest range of potential application from all existing fuel cell systems. PEMFC systems usually operate below 90 °C and have an electric power output between some milliwatts up to some hundred kilowatts [1]. The low temperature range, their ability for fast load changes as well as their comparably fast start-up characteristics make PEMFC very attractive especially for portable or mobile systems and small CHP (combined heat and power) units for distributed power generation [5,6]. Normally PEMFC are operated with pure hydrogen, but options like reformate gas from liquid hydrocarbons (e.g. methanol, natural gas) are possible.

Progress in fuel cell research activities not only led to increased power density and efficiency of fuel cells but also to a variety of preparation techniques and available materials for fabrication. In the literature the following state-of-the-art procedures are known: the so-called indirect decal method, the gas diffusion layer (GDL)-based method and the membrane-based method. For the decal method a transfer film is brushed

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with catalyst ink, dried and hot pressed onto the electrolyte film [7–9,24]. The GDL-based method implies, that the catalyst ink is directly painted or sprayed onto the GDL and then hot pressed onto the membrane [10–13]. Fabricating the MEA with the membrane-based method usually consists of spraying the catalyst ink directly onto a dry, blank, hot and fixed membrane followed by a curing or hot pressing step [14–17]. The latter two methods have the advantage, that the catalyst loading can be adjusted very precisely by simply weighing the MEA (or the GDL) before and after coating with the catalyst ink. Applying the electrodes by the decal method contains the risk of uneven or incomplete catalyst transfer from the transfer film to the membrane. For that reason we restricted our investigations to the GDL- and membrane-based method.

A previous investigation was carried out in order to optimize the combined procedure of catalyst ink spraying onto a membrane followed by a hot pressing procedure with the GDL layer [18,19]. The aim of this previous work was to identify the influence of some process parameters of these two methods that are interdependent. The optimized results were used in the present work. The considered parameters were spraying pressure and distance; air to ink ratio; membrane temperature during spraying; press temperature, time and pressure. Considering the high number of interdependent variables, the data were treated electronically by statistical software (Plackett-Burman factorial design, StatSoft Inc., STATISTICA, Version 5.1) and the response surfaces were obtained, showing optimized results [18].

The objective of this work was to study differences in fuel cell performance resulting from different preparation procedures and to identify an optimized fabrication concept with regard to maximal performance, considering the previous optimized procedure.

2. Experimental details

2.1. Catalyst ink preparation

The 20 wt.% Pt supported on carbon black catalyst from E-TEK was used in all experiments for both cathode and anode. Our standard ink preparation consisted of first adding Millipore water to the catalyst in a weight ratio 20:1 to get an ink that can be sprayed. Then a water-based 10 wt.% Nafion solution from DuPont (SE-10072) was directly added to the catalyst/water slurry. The Nafion content in the dry electrodes was 35 or 50 wt.%, respectively. For a good mixing of Nafion, the ink was stirred thoroughly with a magnetic stirrer overnight. For some MEAs the ink preparation was modified, e.g. the ink was stirred additionally in an ultrasonic mixer or the ink composition was altered by using acetone as solvent instead of Millipore water ("acetone-based ink").

2.2. Fabrication of the membrane electrode assembly

Nafion 105 polymer electrolyte membranes from DuPont were used for all experiments. After cutting, the samples were cleansed and treated in the following way to ensure that the membrane is completely in the protonic form: boiling in 3 wt.% H_2O_2, cleaning in approximately 100 °C hot Millipore water, boiling in 0.5 M H_2SO_4 and cleaning in hot Millipore water again. Each cleaning step took approximately 1 h.

An aluminum frame was used to fix the wet, swollen Nafion film or the GDL, depending on whether the electrolyte film or the GDL was sprayed with catalyst. After drying in an oven (90 °C), the frame was placed on a vacuum-heating table (120 °C) and weighed regularly till constant weight. An airbrush gun was used for catalyst application. Usually, the catalyst ink was sprayed in layers directly onto the membrane till the desired catalyst loading. Only when noted explicitly the catalyst was sprayed onto the GDL. The temperature of the heating table was adjusted to 120 °C. This allowed fast and uniform drying of the sprayed water-based ink. MEAs that were prepared by using an acetone-based ink were sprayed at a lower temperature (70 °C). Again, the weight was controlled by regular measurements after drying of each layer that was sprayed. The catalyst loading was adjusted to 0.4 mg/cm^2 on the anode and 0.6 mg/cm^2 on the cathode. Both electrodes had an active surface area of 25 cm^2.

After fabrication, the MEA was pressed either together with or without gas diffusion layers at 127 °C, 2 bar and annealed at 135 °C, 30 min. Some MEAs were only heat treated without pressing. Two different kinds of GDLs were used: carbon cloth (EC-CC1-060T, 1.75 g/cm^2, 0.33 mm thickness) or Toray graphite paper (EC-TP1-060T, 0.49 g/cm^2, 0.17 mm thickness) both delivered from ElectroChem. All GDLs were teflonized with a Teflon loading of 35%.

2.3. Single cell testing

The MEAs were sandwiched between two GDLs (if not already pressed together with GDLs) and then installed in a graphite single cell with serpentine flowfield (ElectroChem). After holding the cell for 2 h at a cell voltage of 600 mV, polarization curves from high to low current density were measured. All cells were operated with humidified H_2 (T_{hum} = 80 °C) and dry O_2 at a cell temperature of 65 °C with ambient pressure on the anode and cathode side. The conversion of oxygen and hydrogen was kept constant at 50% over the whole current density range except for current densities below 160 mA/cm^2 where H_2 and O_2 flow were no longer reduced. A Dynaload (TDI model RBL 488) was used as electric load for the polarization measurements. Electrical impedance spectroscopy (EIS) was applied to get further insight into the effects of different MEA preparation techniques (dU = 5 mV, 100 mHz–10 kHz). The EIS setup was delivered from GAMRY Instruments and consisted of a FC350 Fuel Cell EIS System coupled to a PC4 Potentiostat/Galvanostat

System connected to the electronic load for on-line EIS experiments. The fuel cell test station used was built at the Energy and Nuclear Research Institute in São Paulo, Brazil.

3. Results and discussion

3.1. Prefabricated MEAs with differently applied GDLs from Toray paper and carbon cloth

Various techniques for the application of the GDLs were examined. All methods have in common, that the MEAs where always prefabricated by spraying and drying the catalyst ink on the Nafion membranes and that only the after-treatment like pressing or annealing was different. Three different techniques were examined with Toray paper as GDL:

(A1) Hot pressing of the prefabricated MEA only. Toray paper was inserted into the test cell together with the pressed MEA.
(B1) Hot pressing of the prefabricated MEA together with Toray paper.
(C1) Annealing of the prefabricated MEA only. Toray paper was again inserted during the assembly of the test cell.

The best result for MEAs with Toray paper as GDL was obtained when the membrane electrode unit was hot-pressed only (Method A1). Fig. 1 shows that at 600 mV this cell delivered a current density of 671 mA/cm^2, which corresponds to a power density of 0.40 W/cm^2. The lowest performance with 0.16 W/cm^2 at 600 mV was observed for the MEA that was fabricated by pressing the membrane with electrodes and Toray paper together (Method B1).

Pressing might cause structural changes in the Toray paper, which reduces electrical conductivity of the GDL. We have investigated these effects by electrical impedance spectroscopy (EIS). The cell resistances were obtained from the

Fig. 2. Impedance spectroscopy of single MEAs with Toray paper as gas diffusion layers that were prepared by different preparation techniques: pressed without GDL (A1), annealed without GDL (C1) and pressed together with Toray GDL (B1). $T_c = 65\,°C$, $T_{hum} = 80\,°C$ at anode, ambient pressure on anode and cathode, $i = 40$ mA/cm^2.

value of the intersection of the high frequency impedance part with the Re-axis, where the Im part is equal to zero. Fig. 2 demonstrates that the MEA that was prepared by pressing the membrane electrode unit and Toray paper together exhibits the highest ohmic resistance of approximately 0.5 Ω cm^2. Correspondingly, this MEA delivered the poorest power density. The MEA with the highest performance (pressed without Toray) has the lowest cell resistance of approximately 0.17 Ω cm^2. As all parameters except pressing were kept constant, this can most likely be ascribed to a modified structure of the GDL. Broken graphite fibers and interrupted electronic pathways caused by GDL pressing may lower its conductivity. In contrast, pressing only the membrane with electrodes might produce compressed electrodes with higher electronic conductivity. This reduces the ohmic resistance of the whole MEA [20,21]. However, it has to be noted that the GDL resistance is just one part of the overall cell resistance. The MEA
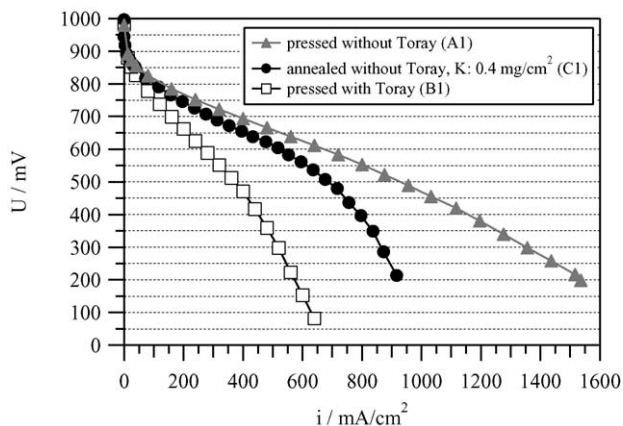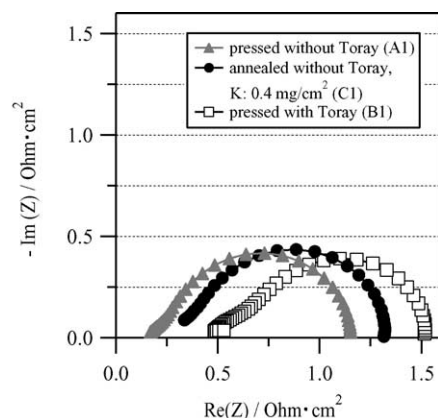
Fig. 1. Cell voltage vs. current density of single MEAs with Toray paper as gas diffusion layers that were prepared by different preparation techniques: pressed without GDL (A1), annealed without GDL (C1) and pressed together with Toray GDL (B1). $T_c = 65\,°C$, $T_{hum} = 80\,°C$ at anode, ambient pressure on anode and cathode.
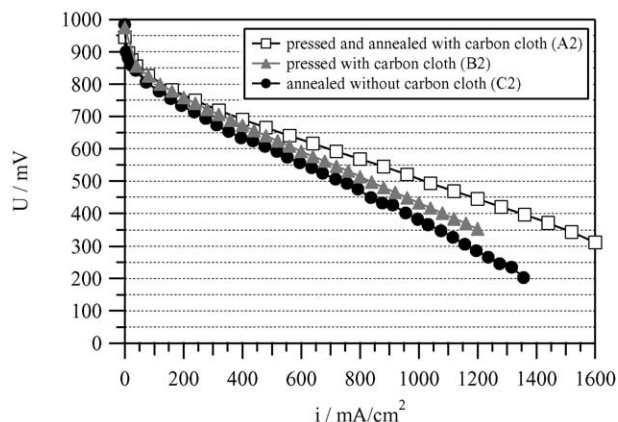
Fig. 3. Performance of single MEAs with carbon cloth as gas diffusion layers, prepared by different techniques: pressed and annealed with GDL (A2), pressed with GDL (B2) and annealed without GDL (C2). $T_c = 65\,°C$, $T_{hum} = 80\,°C$ at anode, ambient pressure on anode and cathode.

resistance obtained by EIS at the high frequency intercept is the sum of all ohmic resistances in the cell (contact, electrolyte, etc.) [21]. Hence, pressing the GDL may influence the cell resistance also indirectly, e.g. changed hydrophobicity and slower water diffusion in the GDL may additionally increase the electrolyte membrane resistance.

As alternative to Toray paper, carbon cloth was investigated as GDL. Carbon cloth is cheaper and more robust, which is advantageous for handling. Again, three different methods of GDL application were studied:

(A2) Hot pressing and consequent annealing of the prefabricated MEA together with carbon cloth.
(B2) Hot pressing of prefabricated MEA together with carbon cloth.
(C2) Annealing of prefabricated MEA only. Carbon cloth was inserted into the test cell together with the pressed MEA.

The results show that very good power densities up to 0.41 W/cm^2 at 600 mV can also be achieved with carbon cloth as GDL. Fig. 3 illustrates that differences among the three chosen MEA fabrication techniques with carbon cloth is not as pronounced as with Toray paper. Opposite to Toray paper, better performances were obtained when the GDL was
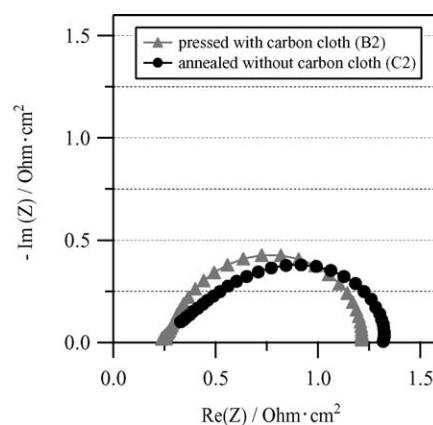

Fig. 4. Impedance measurements of single MEAs with carbon cloth as gas diffusion layers that were prepared by different preparation techniques: pressed with GDL (B2) and annealed without GDL (C2). $T_c = 65\,^\circ$C, $T_{hum} = 80\,^\circ$C at anode, ambient pressure on anode and cathode, $i = 40$ mA/cm^2.

hot-pressed together with the MEA (Method B2). Subsequent annealing increased the power density even further (Method A2). Pressing the carbon cloth seems not to reduce its conductivity (Fig. 4), hydrophobicity or ability for water diffusion. It is likely, that pressing even increases conductivity or reduces
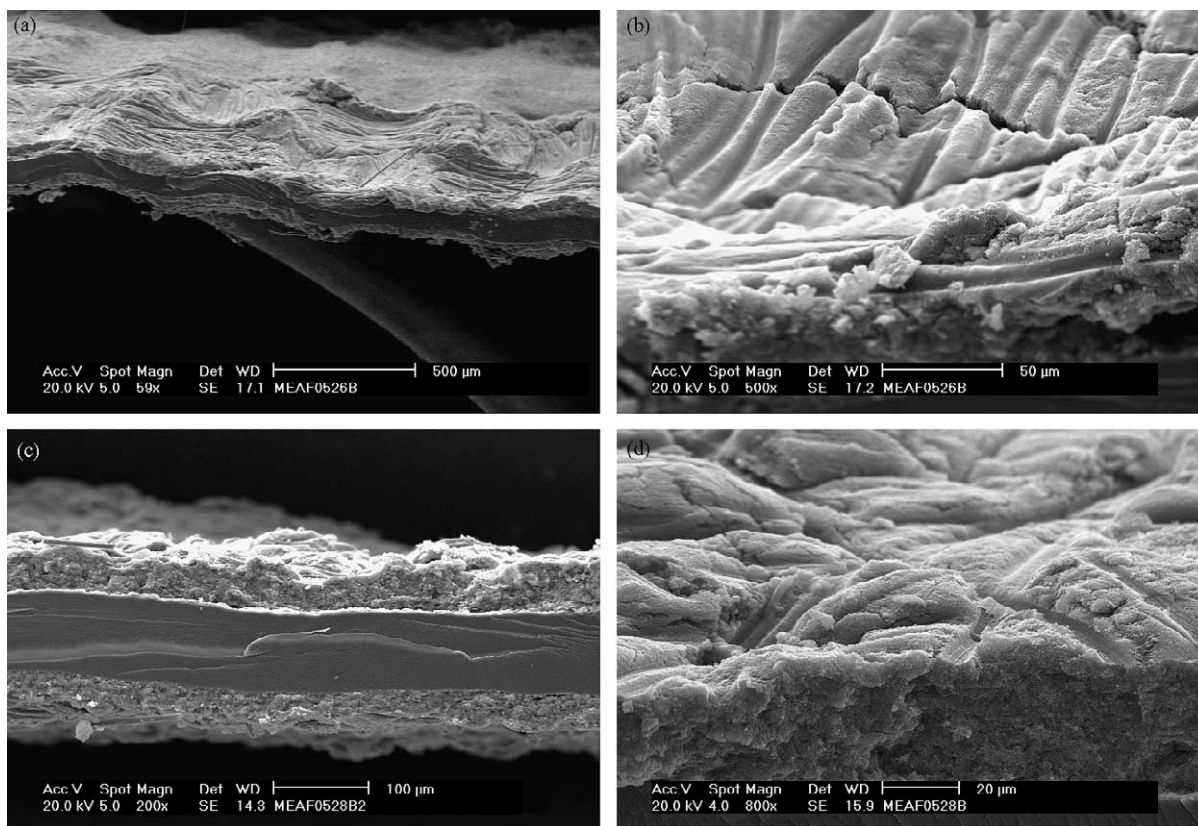

Fig. 5. (a) MEA was pressed together with carbon cloth during fabrication; GDL was removed after fracturing, 50× magnification; (b) electrode surface of MEA that was pressed together with carbon cloth during fabrication; GDL was removed after fracturing, 500× magnification; (c) MEA was pressed together with Toray paper during fabrication; GDL was removed after fracturing, 200× magnification; (d) electrode surface of MEA that was pressed together with Toray paper during fabrication; GDL was removed after fracturing, 800× magnification.

contact resistance between electrode and GDL. In contrast to Toray paper, carbon cloth is flexible, its fibers are not brittle and therefore its structure does not change during pressing.

SEM pictures of MEAs that were fractured in liquid nitrogen show that their structure and electrode surface look different depending on whether they had been contacted with Toray paper or carbon cloth. Carbon cloth that was pressed together with the MEA transfers its woven structure onto the whole MEA (Fig. 5a). Thus, the electrical contact between electrode and GDL is probably enhanced. In Fig. 5a and b the electrode surface is almost completely imprinted from carbon cloth fibers. In contrast, Toray paper with its relatively smooth surface compared to carbon cloth has less impact onto the electrode surface, also after pressing. Inferior contact between GDL and electrode is assumed because fewer imprints of fibers can be discerned in Fig. 5d.

3.2. Modification of Nafion content in the electrode

A Nafion content of approximately 35 wt.% was found to be optimal in preliminary investigations [21,22]. However, the optimal Nafion content in the porous electrode depends on the electrode morphology and, consequently on the electrode producing method. As illustrated in Fig. 6, it is clear that a higher Nafion content leads to a somewhat better performance in fuel cell measurements concerning the described MEA producing technique. This behavior is observed regardless whether Toray paper or carbon cloth is used as GDL.

3.3. Influence of spraying the catalyst layer onto the GDL or onto the electrolyte membrane

Two direct methods for applying the electrodes are common: the membrane-based method with application of the catalyst ink directly onto the membrane and the GDL based-method, where the ink is applied onto the GDL by spraying or painting. We have examined and compared both direct meth-

Fig. 7. Performance of single MEAs with carbon cloth as gas diffusion layers that were prepared by spraying either onto the membrane or onto the GDL. The 35% Nafion in electrode, $T_c = 65\,°C$, $T_{hum} = 80\,°C$ at anode, ambient pressure on anode and cathode.

ods with carbon cloth. The ink was sprayed either onto the GDL or onto the membrane directly.

A current density of approximately $830\,mA/cm^2$ at $600\,mV$ with a peak power of $0.58\,W/cm^2$ at $450\,mV$ was recorded for the MEA that was prepared by pressing the catalyzed GDLs containing 35% Nafion in the electrode onto the electrolyte film (Fig. 7). This represents the best result for all carbon cloth MEAs and is even 24% better than the best result for a MEA with Toray paper. The result is especially surprising because this MEA also outperforms the MEA with directly applied ink onto the membrane. The carbon cloth GDL used was not equipped with a carbon micro-layer. Therefore, it was expected that catalyst particles penetrate into the open pore structure of the cloth during spraying. Less catalyst should be part of the electrochemical active electrode and as consequence of the loss of catalyst particles one would expect a lower performance. Such a behavior like this was only observed for electrodes with 50 wt.% Nafion (Fig. 8) and not
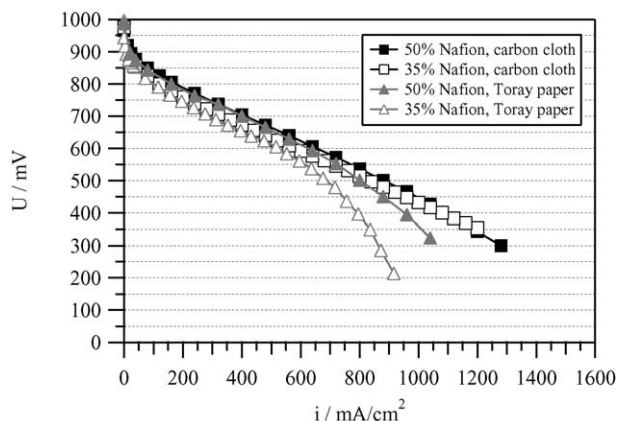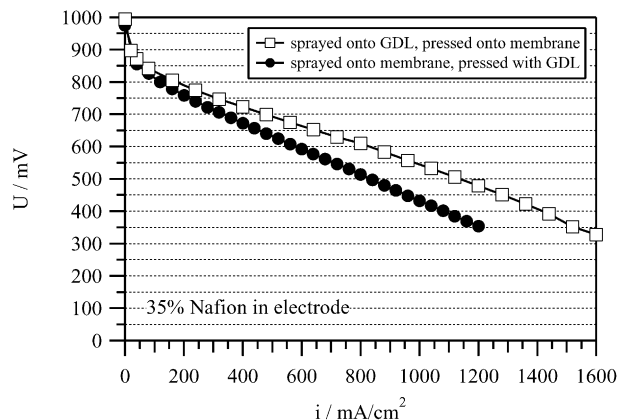

Fig. 6. Performance of MEAs with 35 and 50 wt.% Nafion content, respectively. Toray MEAs were only annealed, carbon cloth MEAs hot pressed with the GDL. $T_c = 65\,°C$, $T_{hum} = 80\,°C$ at anode, ambient pressure on anode and cathode.
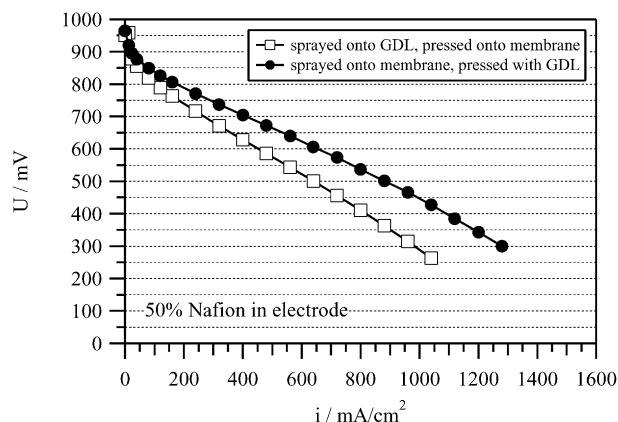

Fig. 8. Performance of single MEAs with carbon cloth as gas diffusion layers that were prepared by spraying either onto the membrane or onto the GDL. The 50% Nafion in electrode, $T_c = 65\,°C$, $T_{hum} = 80\,°C$ at anode, ambient pressure on anode and cathode.

for electrodes with 35 wt.% Nafion, however. This result also confirms the dependence of the optimized Nafion content on the electrode morphology. Further investigations need to demonstrate whether the use of GDLs with carbon micro layers results in additional power improvements in combination with this preparation technique.

3.4. Modification of the solvent in catalyst ink

Normally the solvent used for the ink preparation is a water-based solution, but some organic solutions are also employed [12,17,23]. Water is not harmful, cheap and not reacting with the catalyst (no ignition, no poisoning). However, water has some drawbacks with regard to the ink application process. The airbrushing gun is particularly prone to congestion with catalyst slurry when a water-based ink is used. Furthermore, the Nafion membrane starts swelling very extensively when it comes into contact with the liquid, water-based spray. Therefore inks with acetone instead of water were investigated. Only the solvent was changed and the ink formulation was not modified otherwise. Acetone is an excellent solvent and highly volatile at much lower temperatures than water. No ignition was observed when it gets in contact with catalyst, neither during preparation nor spraying of the ink. With the acetone-based ink no gun congestion occurred during spraying, because of a "self-cleaning" effect. Thus, the ink could be sprayed very precisely and homogenously. Swelling of the membrane was reduced significantly, even at much lower spraying temperature for acetone-based inks (70 °C, water-based inks: 120 °C). The MEA dries much more quickly, resulting in faster constant weight and thereby speeding up the fabrication process. Another positive effect is that the catalyst loading can be adjusted much more accurately. Fig. 9 illustrates that the performance can be increased when spraying an acetone-based ink onto the membrane. Spraying onto the GDL resulted in slightly poorer perfor-

mance, maintaining the described advantages of the acetone-based ink for MEA fabrication, however.

4. Conclusion

In this study the effects of different membrane electrode assembly fabrication parameters on the PEMFC performance were investigated. Toray paper and carbon cloth as well as the fabrication of the whole GDL/MEA assembly by different techniques, e.g. pressing only MEA or MEA and GDL together, were compared. Further parameters that were investigated include: variation of Nafion content in the electrodes, influence of spraying the catalyst layer onto the GDL or the electrolyte membrane and solvent modification in the catalyst ink. The best performance with approximately $830\,\mathrm{mA/cm^2}$ at 600 mV was obtained, when the electrodes were prefabricated by spraying of the catalyst ink on carbon cloth as GDL, followed by hot pressing the GDL electrode assembly onto the membrane. Ongoing investigations need to reveal differences among differently prepared MEAs with regard to their long-term stability. For example, delamination of the MEAs has not been observed in 500 h investigations, but might occur after much longer fuel cell operation. This is an important issue with respect to longevity and long-term performance.
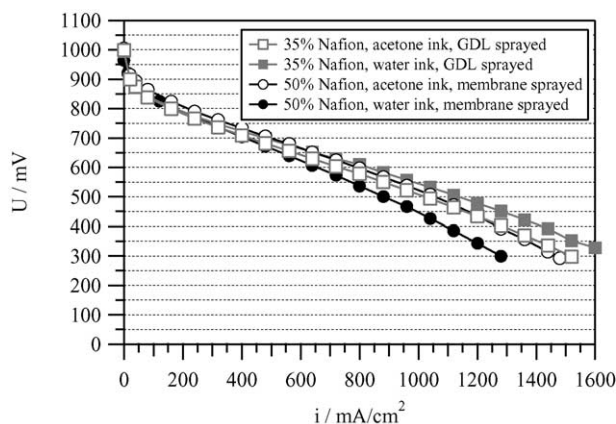
Fig. 9. Performance of single MEAs with carbon cloth as gas diffusion layers. Catalyst inks were either water-based or acetone-based and sprayed onto the membrane or GDL, respectively. All MEAs were pressed together with the GDL. $T_c = 65\,°C$, $T_{hum} = 80\,°C$ at anode, ambient pressure on anode and cathode.

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