Membrane electrode assemblies for unitised regenerative polymer electrolyte fuel cells

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Abstract

Membrane electrode assemblies for regenerative polymer electrolyte fuel cells were made by hot pressing and sputtering. The different MEAs are examined in fuel cell and water electrolysis mode at different pressure and temperature conditions. Polarisation curves and ac impedance spectra are used to investigate the influence of the changes in coating technique. The hydrogen gas permeation through the membrane is determined by analysing the produced oxygen in electrolysis mode. The analysis shows, that better performances in both process directions can be achieved with an additional layer of sputtered platinum on the oxygen electrode. Thus, the electrochemical round-trip efficiency can be improved by more than 4%. Treating the oxygen electrode with PTFE solution shows better performance in fuel cell and less performance in electrolysis mode. The increase of the round-trip efficiency is negligible. A layer sputtered directly on the membrane shows good impermeability, and hence results in high voltages at low current densities. The mass transportation is apparently constricted. The gas diffusion layer on the oxygen electrode, in this case a titanium foam, leads to flooding of the cell in fuel cell mode. Stable operation is achieved after pretreatment of the GDL with a PTFE solution.
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1. Introduction

Regenerative polymer electrolyte fuel cells (RFC) can be operated as an electrolyser splitting water into hydrogen and oxygen with the help of electric energy. The same set-up works as a fuel cell supplying electric power when fed with hydrogen and oxygen or air.

RFCs offer a solution where long term energy storage is required for example in off-grid power supply systems powered by solar energy or uninteruptible power supply systems (UPS). In autonomous systems with surplus energy during high solar radiation in summer, an RFC system can produce hydrogen and oxygen which is stored in tanks. If there is a lack of energy, the unit is fed with the stored gases operating in fuel cell (FC) mode to produce electricity. The evolving water is recycled in order to realise a closed system with low maintenance requirements. In a UPS system, the RFC is run in electrolyser (EL) mode from the grid. In case of a failure of the mains, RFC is switched to fuel cell mode to supply energy.

It has to be mentioned that in both applications RFC is not meant to fully replace batteries, but to overcome problems of long-term energy storage. The advantage compared to batteries is a non-existant self-discharge of RFCs and the chance to store great quantities of energy which can be converted to electricity. However, the round-trip storage efficiency of electricity is still lower than that of batteries. Thus, an improvement in the efficiency of RFCs is necessary [1].

The work described in this article aims at the optimisation of the MEA for regenerative fuel cells. The main problems to be solved in an RFC are [2–5]:

- Cell potentials of 1.6–2 V in electrolysis mode together with O$_2$ in statu nascendi which is highly reactive lead to a

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Nomenclature

b	Tafel slope (mV decade^{-1})
C_{dl}	double layer capacitance (mΩ)
F	Faraday constant (C mol^{-1})
i	current density (A m^{-2})
i_o	exchange current density (A m^{-2})
R_{el}	resistance (mΩ)
R_{ct}	charge transfer resistance (mΩ)
t	time (min)
T	Temperature ($^\circ$C)
$\tilde{U}$	ac voltage (V)
U	dc voltage (V)
Z	ac impedance (mΩ)

Greek letters

λ	stoichiometry (−)
η	overvoltage (mV)
ε	efficiency (−)
ω	frequency (s^{-1})

corrosive atmosphere. Thus, materials at the O_2 electrode have to be corrosion resistant.

- Hydrophobic behaviour of the gas diffusion layer (GDL) is difficult to achieve with the non-corrosive material. Flooding of the pores results in severe performance loss during fuel cell operation. On the other hand, the use of highly hydrophobic GDLs hinders water transport to the electrode during electrolysis. Thus, a compromise has to be achieved between stable fuel cell and electrolyser operation mode.
- Part of the gases permeates through the membrane to the opposite electrode where it reduces the cell potential [7]. Preparation methods for membrane electrode assemblies (MEA) have to be improved that reduce the permeation of gases through the membrane.

In the work presented MEAs are developed for RFC application. The aspects under which the MEA preparation have been modified are:

- Hydrophobicity: In EL mode hydrophobic behaviour of the electrode and/or GDL reduces the performance of the cell, as water cannot reach the reaction zone easily. In FC mode, flooding of the cell is prevented.
- Polishing of the membrane: Polishing of the membrane enhances the adhesion of the electrode on the membrane which is important to obtain low degradation over time. On the other hand, membrane thickness is slightly reduced which influences the gas permeation rate through the membrane.
- Additional coating with Pt: An additional layer of Pt is sputtered on the membrane and the electrode, respectively in order to increase the gas quality in EL mode and reduce losses due to gas cross-over in FC mode.

The prepared MEAs are investigated at 5–80 $^\circ$C, 1–8 bar and 100–200 mA cm^{-2}.

2. Experimental

2.1. Experimental set-up

A single cell with 49 cm^2 active area is used to characterise the MEAs. The assembly is shown in Fig. 1. The flow field plates are manufactured from titanium and have a parallel channel structure. The end plates have channels for heating/cooling liquid to control the cell temperature and apply a unitized clamping pressure. The MEA is placed between the flow fields. Gas diffusion layers allow the distribution of the reactants and the current flow over the active area.

In electrolysis mode a carbon paper GDL (Toray 060) is installed at the hydrogen side, a titanium foam is used at the oxygen side, which is stable at the high potential. In fuel cell mode different GDLs were applied (see Section 2.3).

The test cell is operated in the experimental set-up displayed in Fig. 2. Gas supply for fuel cell operation is controlled via mass flow meters (gas control system PR 4000 F, MKS Instruments). Temperature controlled humidifiers humidify the gases to 100% RH at operation temperature. In order to avoid condensation gases pass through heated pipes before entering the RFC. Temperatures are controlled via a temperature controller (Universal Digital controller 238, Tecon). Water for electrolyser mode is supplied from water supply tanks. Pressure reducers at the gas outlet allow the variation of operation pressure. The electronic load (7141-Z, ITS) is used for fuel cell operation. Power for electrolysis is supplied from a constant power supply (6012A, Hewlett Packard). A high frequency ohmmeter (4328A, Hewlett Packard) determines the ac impedance at 1 kHz of the cell, the current is measured using a shunt type HA5050 with a resistance of 1 mΩ. The data acquisition system is GBD, Delphin. A constant temperature of the cell is realised using a cryostat (753, Fischerbrand) which circulates water through the end plates of the cell for heat supply and dissipation, respectively.
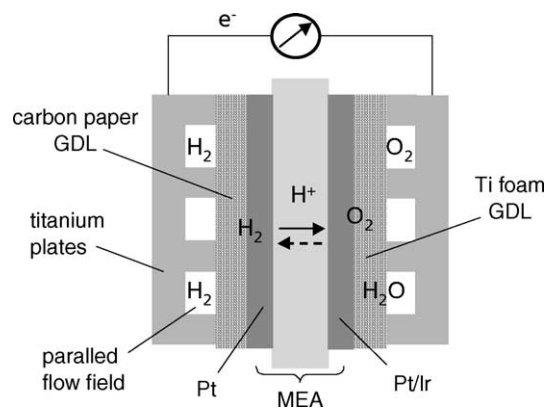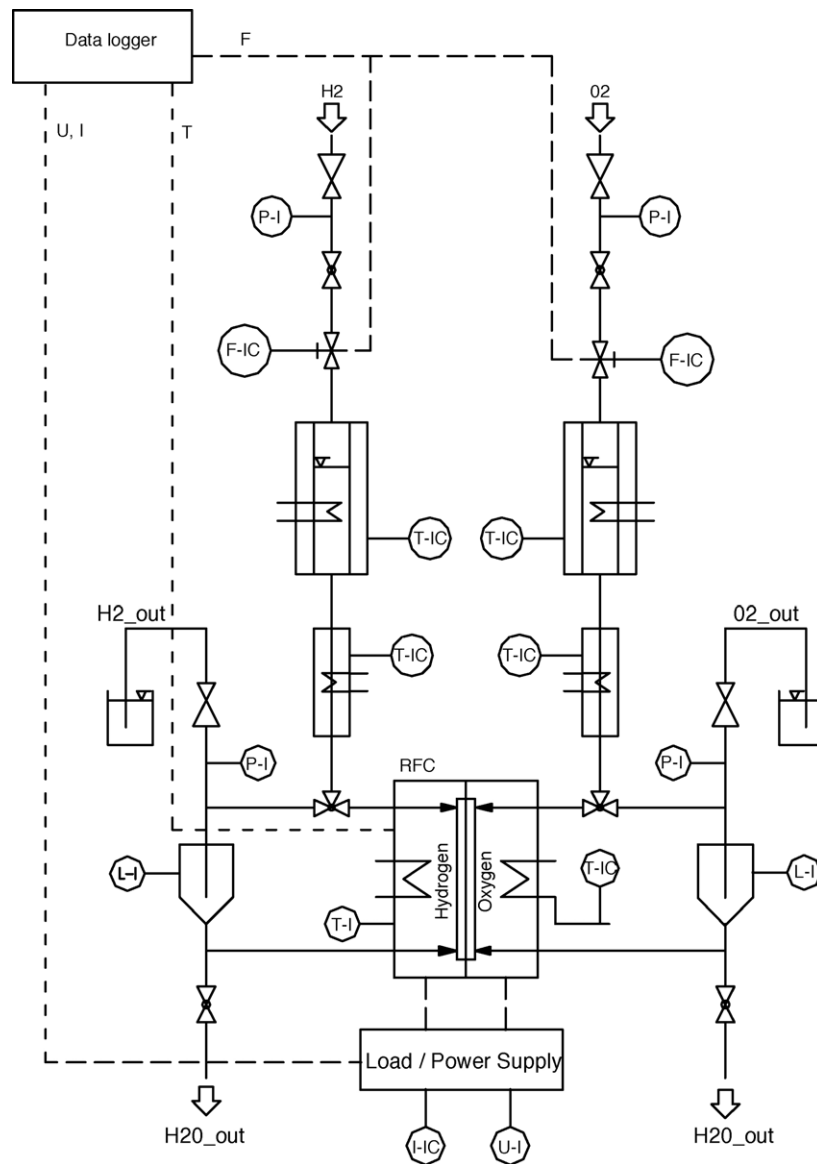

Fig. 1. Schematic diagram of a RFC.

Fig. 2. Experimental set-up.

Additionally, the gas quality can be analysed by a mass spectrometer.

2.2. Preparation of MEAs

The standard procedure to prepare the MEAs is the Decal method as described in previous work [3–5,10]. Platinum black powder for the hydrogen electrode and a 1: 1 mixture of platinum and fine iridium black powder for the oxygen electrode are used as catalyst. For each electrode an amount of $2\,mg\,cm^{-2}$ catalyst is dissolved in deionised water and dispersed in an ultrasonic bath. The dispersion is sucked through a filter paper, which forms the pre-stage electrode. After drying, the resulting catalyst layer is sprayed with 5% Nafion® suspension to guarantee a good contact between electrode and electrolyte. The electrodes are then pressed on a pre-

treated Nafion® 117 membrane at $130\,°C$ with a pressure of $2.2\,kN\,cm^{-2}$. The adhesion of the catalyst layer can be further improved by polishing the membrane prior to the pretreatment described above. This is done using abrasive paper with a grain size of $320\,\mu m$ applying a defined weight.

To increase the catalyst utilisation and, thereby, the power density of the electrodes, the water management must be optimised. This can be adjusted by placing hydrophobic particles in the porous structure of the electrodes. For the first variation the pre-stage oxygen electrode were dunked into 10% PTFE dispersion for 2 min, dripped and then dried at $110\,°C$ for 20 min.

To increase the hydrogen impermeability, a second variation was made by sputtering an additional layer of platinum on the pretreated Nafion® 117 membrane. Therefore, a plasma is ignited in an argon atmosphere of 0.03 mbar and hold for
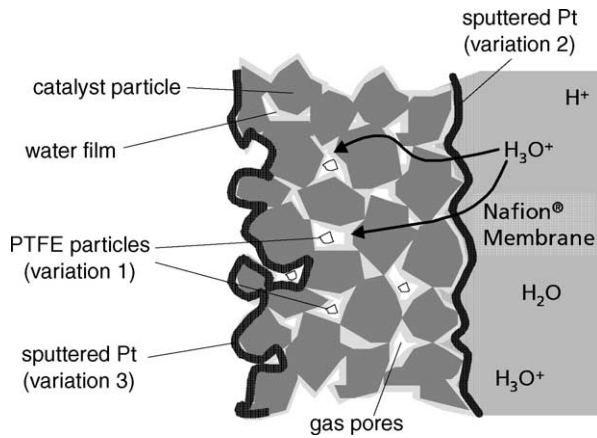
Fig. 3. Schematic exposition of a hot pressed electrode. A thin water film has to cover the catalyst surface to guarantee the proton flow. PTFE particles in the electrode structure will keep the gas pores free from reaction water. Sputtered platinum on the membrane enhances the impermeability. Sputtered platinum on the catalyst increases the power density.

Table 1
Overview of investigated MEAs

MEA02	Standard, polished membrane
MEA03	Standard + hydrophobic O_2 electrode
MEA05	Standard + Pt sputtered on membrane (O_2 side)
MEA06	Standard + Pt sputtered on O_2 electrode

3 min with a current of 40 mA. The resulting layer thickness is approximately 140 nm. The same platinum layer was sputtered to create the third variation, this time on the finished oxygen electrode. Fig. 3 shows a schematic drawing of a hot pressed electrode with variations. Table 1 gives an overview of the different MEAs.

2.3. Conditioning of GDLs

To overcome the water management problems that occur due to the hydrophilic character of the titanium foam in fuel cell mode, experiments to achieve hydrophobic properties were carried out. Thereby, the structure was treated twice for 2 min with 10% PTFE dispersion. Subsequent drying in an ultrasonic bath, sintering at 350 °C for 20 min and hot pressing on the MEA showed homogeneous hydrophobicity of the GDL sample.

To investigate the performance of the MEAs in fuel cell mode, commercial hydrophobic carbon paper (20 BC, SGL Technologies GmbH) is used as GDL to guarantee reproducibility.

3. Results and discussion

3.1. Characterisation of MEAs with polarisation curves

Characterising the above-mentioned modifications of the MEA preparation lead to the polarisation curves shown in
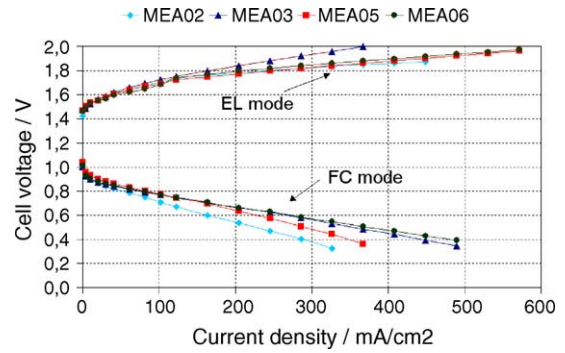

Fig. 4. Polarisation curves of different MEAs in EL and FC mode. Recorded at 50 °C, 1 bar, $\lambda_{O_2} = 1.5$, $\lambda_{H_2} = 1.5$. MEA02: standard, MEA03: hydrophobic oxygen electrode, MEA05: Pt sputtered on membrane, MEA06: Pt sputtered on oxygen electrode.

Fig. 4. In electrolysis mode, only for MEA03 (with a hydrophobic oxygen electrode) a difference in the polarisation curve is observed. The PTFE particles hinder the transport of water to the catalyst surface resulting in a decrease of the power density in EL mode. Additional platinum sputtered on the membrane (MEA05) or electrode (MEA06) shows little influence on the performance in electrolysis mode.

In fuel cell mode each variation increases the power density: Sputtered Pt on the membrane (MEA05) shows the highest voltage at current densities below 100 mA cm^{-2}. MEA03 with hydrophobic O_2 electrode displays stable operation at current densities up to 500 mA cm^{-2}. With an additional layer of sputtered Pt on the oxygen electrode MEA06 shows the best performance in fuel cell mode.

In order to get more detailed information on the electrochemical activity of the different MEAs, the experimental data gained from FC mode were used to determine the Tafel slope b. Using the Tafel equation (see (1)), the activation overvoltage η_a can be calculated as follows [8]:

$$\eta_a = b \log\left(\frac{i}{i_0}\right) \tag{1}$$

with the exchange current density i_0 and the Tafel slope b. In Table 2 the Tafel slope as well as the exchange current density of the different MEAs are given. MEA03 and MEA06 display the same order of magnitude in the Tafel slope (47 and 50 mV decade^{-1}, respectively). An enhancement can be clearly observed compared to the standard MEA (MEA02) with a Tafel slope of 67 mV decade^{-1}. In fuel cell mode, the increased hydrophobicity of the electrode (MEA03) enhances the electrochemical activity of the electrode. The additional

Table 2
Tafel slope and exchange current density of different MEAs in FC mode, determined from polarisation curves

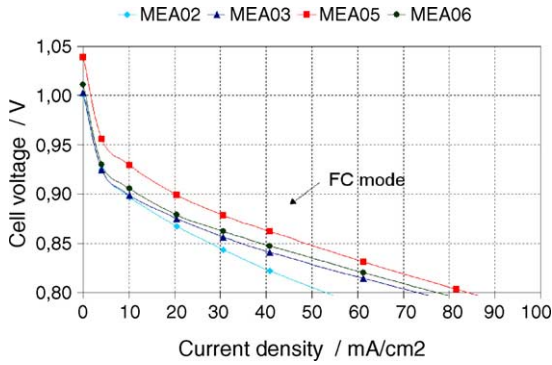| MEA	b (mV decade^{-1})	i_0 (μA cm^{-2})
MEA02	67	970.7
MEA03	47	978.8
MEA05	65	972.2
MEA06	50	977.7

Fig. 5. Polarisation curves of different MEAs in FC mode at low current densities (50 °C, 1 bar, $\lambda_{O_2} = 1.5$, $\lambda_{H_2} = 1.5$). MEA02: standard, MEA03: hydrophobic oxygen electrode, MEA05: Pt sputtered on membrane, MEA06: Pt sputtered on oxygen electrode.

Pt layer intending a reduction of gas permeation through the membrane shows a positive effect only if sputtered on the electrode (MEA06). Both variations (hydrophobic treatment and sputtering of Pt on the oxygen side) show the same influence on the exchange current density which is a measure effective area of the electrode. Pt sputtered on the membrane (MEA05) has no positive effect on fuel cell performance apart from an increase in open cell voltage (see Fig. 5). This indicates a reduced hydrogen content at the cathode (see Section 3.2).

3.2. ac impedance spectroscopy

Apart from polarisation curves, ac impedance spectroscopy is used to analyze the influence of variations in MEA preparation at different cell voltages. During ac impedance spectroscopy measurements, the cell is loaded with a constant voltage (U_{load}) superposed by a harmonic oscillation of small amplitude (ΔU) with a frequency ω [9,10].

$$\tilde{U}(t) = U_{load} + \Delta U \, \sin(\omega t) \tag{2}$$

For frequencies from 0.2 Hz to 3 kHz, the cell voltage $\tilde{U}(\omega)$ is divided by the response current of the cell to get the impedance $Z(\omega)$ of the cell. The impedance spectra gained from the different MEAs are displayed in a Nyquist plot at an operation voltage of 900 and 600 mV, respectively (see Fig. 6). The lower the voltage of the cell, the higher is the current density and the activation overpotential. This leads to a lower ac impedance. The effect can be observed comparing the spectra at 600 and 900 mV.

At low current densities (i.e. high cell voltages) the ac impedance spectra can be fitted with a simple equivalent circuit (Randle's circuit, see Fig. 7) where the membrane resistance is connected in series with a charge transfer resistance and a parallel connected double layer capacity. The impedance of this equivalent circuit is determined by
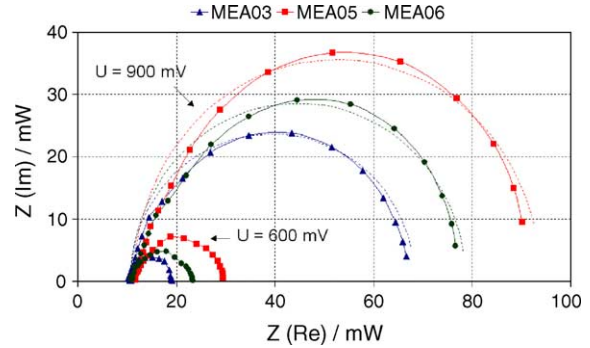

Fig. 6. ac impedance spectra for three different MEAs at 900 and 600 mV. For 900 mV spectra are fitted with a Randle's circuit diagram (dotted lines). Impedances are recorded at $p = 1$ bar, $T_{cell} = 50$ °C, $T_{hum} = 53$ °C, $\lambda_{O_2} = 1.5$, $\lambda_{H_2} = 1.5$.
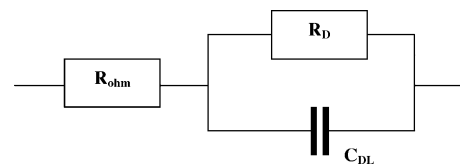

Fig. 7. Randle's circuit diagram.

the following equation [11,12]:

$$Z = R_{el} + \frac{R_{ct} - i\omega R_{ct}^2 C_{dl}}{1 + \omega^2 R_{ct}^2 C_{dl}^2} \tag{3}$$

R_{el} represents all resistances that are not due to the reaction. C_{dl} is the double layer capacity and ω the frequency. In Table 3 the charge transfer resistances for the varied MEAs are given for 900 mV. MEA03 with hydrophobic electrode shows the lowest impedance. An additional layer of sputtered platinum on the electrode seems to have negative effect on the charge transfer. Platinum sputtered directly on the membrane (MEA05) shows the highest impedance. Probably, the proton transport is constricted as visualised in Fig. 3. This assumption also agrees with the interpretation of the Tafel slopes in Table 2.

3.3. Hydrogen gas diffusion through the membrane

The quality of the gases produced in EL mode with a standard MEA was investigated using mass spectrometry. Fig. 8 shows the amount of hydrogen in the oxygen as a function of temperature at different pressure levels for a current density of 100 and 200 mA cm^{-2}, respectively. This is a measure for hydrogen gas diffusion through the membrane. A notable

Table 3
Charge transfer resistance of varied MEAs in FC mode

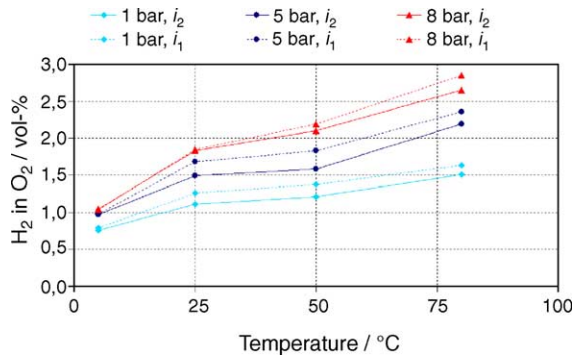| MEA03	47.3 mΩ
MEA05	71.5 mΩ
MEA06	57.2 mΩ

Fig. 8. Hydrogen gas diffusion through membrane for standard MEA (MEA02), analysed by mass spectrometry of produced oxygen gas in EL mode. $i_1 = 100\,\mathrm{mA\,cm^{-2}}$, $i_2 = 200\,\mathrm{mA\,cm^{-2}}$.

amount of hydrogen (up to 3%) was detected, depending on temperature, pressure and current density. A higher current density results in a decrease of the amount of H_2 in O_2 due to a higher gas production rate at a constant gas diffusion rate. As the partial pressure gradient increases with higher operating pressure, more hydrogen migrates through the membrane. In Fig. 9 the gas purity as a function of current density (dashed lines) for the different MEAs are shown together with the polarisation curves in EL mode. Polishing the membrane before MEA preparation to improve the contact with the catalyst layer (MEA02) leads to a clear increase in gas impurity (around 2% H_2 in O_2). All the other membranes were not polished, which leads to a notable reduction in hydrogen content in oxygen down to around 0.8%. With a platinum layer sputtered directly onto the membrane MEA05 shows the highest impermeability, with hydrogen percentage of around 0.5 vol.%. This complies with MEA05 having the highest open circuit voltage in FC mode (1.04 V at 50 °C, 1 bar). The reason for the enhanced impermeability could be a change in structure of the membrane surface due to the sputtering process. The platinum layer on the membrane might also cause an increase in recombination of hydrogen and oxygen to water. Further investigations on the diffusion characteristics of the MEAs are necessary to affirm these assumptions.
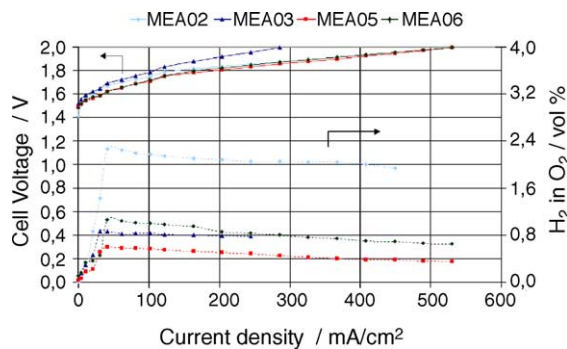

Fig. 9. Polarisation curves (solid lines) and oxygen gas purity (dashed lines) of varied MEAs in EL mode. Recorded at 50 °C and 8 bar.
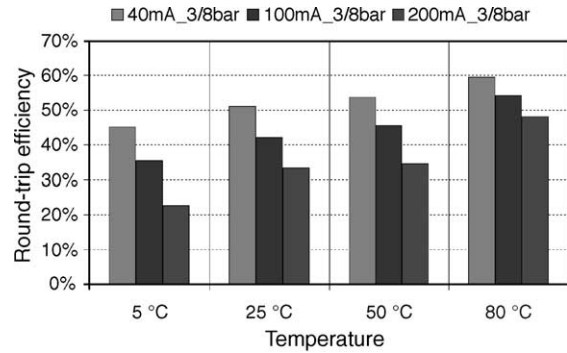

Fig. 10. Round-trip efficiencies of a reversible fuel cell with a standard MEA at a pressure of 3 bar in fuel cell mode and 8 bar in electrolysis mode. Current densities: $i_1 = 40\,\mathrm{mA\,cm^{-2}}$, $i_2 = 100\,\mathrm{mA\,cm^{-2}}$, $i_3 = 200\,\mathrm{mA\,cm^{-2}}$.

3.4. Enhancement of round-trip efficiency

The round-trip efficiency ε_{RT} is used for comparison of the different MEAs since the variations in MEA preparation influence the cell performance in EL and FC mode in a different way. It compares energy gained in FC mode to the energy needed for gas production in EL mode. It can be calculated from the operating voltages in fuel cell and electrolysis mode at the current density i.

$$\varepsilon(i)_{RT} = \frac{P(i)_{FC}}{P(i)_{EL}} = \frac{U(i)_{FC}}{U(i)_{EL}} \tag{4}$$

In Fig. 10 the round-trip efficiency is shown for different temperatures and current densities for the standard MEA (MEA02). Increasing current density leads to decreasing efficiency, caused by cumulative losses of resistances and mass transport. At an operating point of 3 bar in FC mode and 8 bar in EL mode, 50 °C and 100 mA cm^{-2}, which is has been proposed for a RFC system, the round-trip efficiency is around 45%.

In order to analyse variations in the coating process, the relative improvements of the efficiencies of all modified MEAs are plotted in Fig. 11. The improvement is related to the standard MEA at 50 °C, a current density of 100 mA cm^{-2} and at a pressure of 3 bar in fuel cell mode and 8 bar in electrolysis mode. The efficiency in FC (see (5)) and EL (see (6)) mode are calculated related to the standard theoretical cell
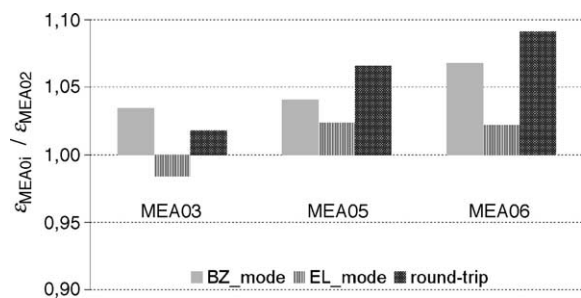

Fig. 11. Round-trip efficiencies related to the standard MEA. Operating point: 50 °C, 3/8 bar, $i = 100\,\mathrm{mA\,cm^{-2}}$.
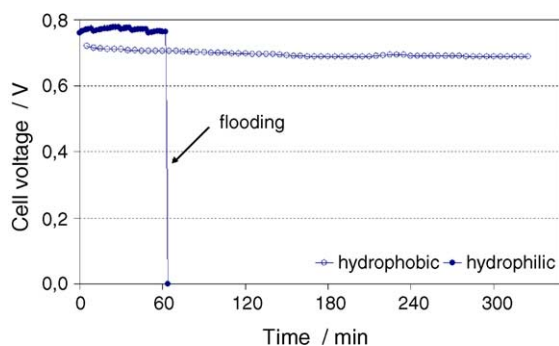
Fig. 12. Experiment with untreated (hydrophilic) and treated (hydrophobic) titanium foam GDL in fuel cell operation $(I_{cell} = 3\,A,\ T_{cell} = 50\,°C,\ T_{hum} = 45\,°C,\ \lambda_{O_2} = 2.5,\ \lambda_{H_2} = 2.0)$.

voltage.

$$\varepsilon_{FC} = \frac{U(i)}{1.23\,V} \tag{5}$$

$$\varepsilon_{EL} = \frac{1.23\,V}{U(i)} \tag{6}$$

MEA03, which shows the lowest activation losses in FC cell mode, has a slightly higher round-trip efficiency since the losses in EL mode are decisive. MEA05 (with sputtered platinum on the membrane) obtains a high the round-trip efficiency. The highest improvement was obtained with MEA06, with sputtered platinum on the oxygen electrode. The main enhancement is caused by the higher fuel cell efficiency: The round-trip efficiency is 4% higher than the one of the standard MEA.

3.5. Effect of treating the titanium foam GDL

The titanium foam GDL which shows excellent operating behaviour in electrolysis mode are also investigated in fuel cell mode, once untreated and once with a hydrophobic treatment (see Section 2.3). The GDL is installed at the oxygen side of the test cell, using a standard MEA (MEA02). In Fig. 12 the cell voltage, loaded with a constant current of 3 A, are shown as a function of time. The cell voltage differs slightly in both measurements which is mainly due to disassembly of the cell between the two measurements. While using a hydrophilic GDL, the reaction water is absorbed from the porous structure. After one hour the pores are flooded, mass transport to the electrode is hindered and the voltage breaks down. With a hydrophobic structure the reaction water is ejected and the gas pores are kept free permanently.

4. Conclusion

MEAs for reversible fuel cells are optimised by modification of the preparation process. Four different MEAs are characterised by polarisation curves, impedance spectroscopy and mass spectrometry.

By treating the oxygen electrode with PTFE dispersion before hot pressing, a notable improvement of the performance in fuel cell mode is obtained. In detailed examinations by polarisation curves and ac impedance spectroscopy, low activation losses can be proved. On the other hand, the performance in electrolysis mode is reduced, supposedly caused by reduced moistening of the catalyst. Best results are obtained by sputtering platinum on the oxygen electrode after hot pressing: An additional layer of catalyst leads to a better performance in both process directions. Thus, MEA06 is the membrane electrode assembly to be preferred for reversible fuel cell applications if high efficiency is aimed at and the additional costs for the sputtered platinum are acceptable.

While characterising the MEAs in electrolysis mode, a remarkable percentage of hydrogen in the produced oxygen gas is observed. An improvement of the impermeability is obtained by hot pressing without polishing the membrane and by sputtering of platinum directly onto the membrane. On the other hand, there is less contact between electrode and electrolyte which leads to a reduced power density at higher current densities.

In long-term operation the GDLs show crucial problems with the water management. Promising results are presented in which the titanium foam GDL is with a hydrophobic dispersion. However, more investigations have to be done to guarantee long-term stability.

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