

On the question of MEA preparation for DMFCs

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Abstract

To get information for the development of a continuous MEA fabrication sequence various preparation strategies are investigated. Diffusion layer suspension is made by magnetic stirring, ultrasound mixing and by use of a ball-mill and the slurry is characterised by particle size measurements. The catalytic layers are applied either to the diffusion backing or directly onto the membrane. The latter method yields to improved MEA performance due to the higher utilisation of the catalytic material. Experiments concerning the influence of the anodic diffusion layer thickness and composition show a strong influence on MEA characteristic. For the anodic diffusion layer the influence of the hydrophobicity on methanol transport and CO₂ removal is investigated by using PTFE or Nafion® as binder. The Nafion® bonded backing shows better mass transport properties for methanol but CO₂ removal becomes crucial at high current densities. Sintering of the PTFE bonded structure improves layer properties for the management of liquid and gas transport. Best results are achieved with sintered PTFE bonded layers with a reduced layer thickness.

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1. Introduction

Fabrication of MEAs for both, H₂-PEMFC and DMFC, is mostly still handwork and therefore accompanied by poor reproducibility, high time effort and a small size of the resulting MEAs. For technical and economical reliability an appropriate fabrication engineering for MEAs has to occur not only in the meaning of electrochemical optimisation but also under the aspects of material processing and conversion. Desirable is a continuous production of electrodes and MEAs to reach more reproducible characteristics and low costs.

Different coating processes for the generation of electrode layers are commonly used. The original method starts with commercially available or self-made diffusion backings where the catalytic active material is applied to, mostly by a spraying- or screen-printing-technique. A stable laminate with the membrane is received by hot-pressing these two-layer electrodes on the ion conducting membrane. Gottesfeld and co-workers [1,2] prepared MEAs by a decal method where a catalytic ink is applied to a PTFE blank and subsequently transferred to the membrane. In another approach the catalyst layer is formed by coating both sides

of the membrane with the catalytic material, leading to a three-layer structure [3,4]. Additional work is done by Gülzow et al. [5,6], using a dry-sprayer for the catalytic coating of the backing or the membrane, combined with a rolling step to bond and fix the functional layers.

A lot of these processes are still in discontinuous operation at laboratory scale or at pilot plants. On the other hand, ink based electrode fabrication methods for PEMFCs have been developed to the point where industry is at the threshold of setting up production plants to manufacture MEAs [7]. Nevertheless, additional basic research and development is indispensable to further improve performance and advance the understanding of electrodes with an higher degree of microscopic structural control.

2. Experimental

The deposition process for the generation of the structural layers is an important engineering aspect. At the ICVT Clausthal, the catalytic layers as well as the microporous diffusion layer, located on a carbon cloth as substrate, are made from an ink composed of carbon black, dispersion agent and binder. This is sprayed by a modified airbrush gun onto the respective substrate until the desired loading is adjusted.

The microporous layer is commonly used to tailor mass transfer properties of the backing. In fact of the two phase

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state of the reaction fluids [8,9] the nature of the porous system becomes a decisive factor for the liquid feed DMFC. To assure good access of oxygen on the cathode and a sufficient removal of CO₂ on the anode the microporous layer is made partly hydrophobic by adding PTFE. At the same time, hydrophilic pores have to manage the removal of excess water (which diffuses from the anode to the cathode) and the generated water has to be removed towards the cathodic flow-field channels. On the anode side the structure has to ensure efficient supply of the active sites with methanol to avoid mass transfer limitations under operation.

2.1. Influence of mixing and milling method on carbon particle size

A homogeneous distribution of carbon and polymer is desirable to guarantee an uniform and porous structure of the diffusion layer for efficient mass transport and electronic conductance in and through-plane. To set the fluid management properties of the backing PTFE is added to adjust the desired hydrophobicity and to bind the carbon. Resulting microporous layers have a pore size on the order of the carbon agglomerates, typically between 100 and 500 nm [10]. In fact of this, the particle size distribution of the spray-suspension used for the formulation of the porous structure becomes an important factor for electrode performance. Particle- and pore size distribution and the distribution of the hydrophobic PTFE influences strongly the capability of sufficient gas- and liquid access, electron conductivity and mechanical strength. By choice of the preparation strategy of the suspension these factors can be adjusted suitable and therefore improve MEA characteristic not only in the diffusion limited range. Besides this, the processing and conversion of the materials and suspensions has to be improved to ensure reproducibility and well processable intermediates. Common used preparation by magnetic stirring is difficult to control and leads to problems during the subsequent processing steps by short time of suspension stability and a wide range of the particle sizes. This complicates the choice of a coating technology that is capable of a series production of the structural layers. The mentioned interrelationships demand an engineering approach for all deployed preparation steps.

To investigate the effect of the suspension preparation on the particle size and layer morphology, different mixing and milling techniques for the carbon, dispersion agent and PTFE are examined. Suspensions are prepared by intense magnetic stirring, treatment of the slurry in an ultrasound bath and use of a computer-controlled wet-ball-mill (Dispermat SL-C12, VMA Getzmann GmbH). The ball-mill can be operated either in batch circuit-flow operation or continuous for high volume MEA production. Due to the online recording of the interesting milling parameters power input, rotation speed, torque and temperature this device is well suited for a controlled and reproducible formulation of suspensions.

Initially the carbon (Vulcan XC72, Cabot) is dried and ground in a laboratory high speed mill before *i*-propanol is added as dispersion agent (1 g carbon black in 50 ml *i*-propanol). Five inks are prepared and investigated. Mixing on a magnetic stirring is commonly used and the most simple method to disperse the carbon. On the other hand, control of fabrication parameters is difficult and the specific power input is low. Ultrasound assisted mixing is characterised by increased power input but the results are dependent on parameters like the frequency and the geometric arrangement of the ultrasound source and the sample and therefore sophisticated to adjust. As well as for the mechanical stirring an online control of the parameters is barely possible. In contrast, the dispersion ball-mill is a common used device in industry and consequently well investigated and suitable for a simple up-scaling. Thus, a transfer of research results from laboratory to industrial scale can be done easily. Operation parameters like power input, filling degree and grinding medium can be chosen and adjusted over a wide range resulting in highly flexible preparation conditions.

The following samples are prepared:

- *Sample A*: 30 min intense mixing on a magnetic stirrer.
- *Sample B*: 30 min intense mixing on a magnetic stirrer and 15 min treatment in an ultrasonic bath.
- *Sample C*: 30 min ball-milling at constant power input.
- *Sample D*: 45 min ball-milling at constant power input.
- *Sample E*: 30 min ball-milling at constant power input, adding of 15 wt.% PTFE after 5 min milling.

For the ball-milled samples the power input is set to 450 W for an overall liquid volume of 830 cm³, as grinding medium quartz glass beads with a diameter of 0.6–0.8 mm (MiniBeads, Mühlmeier GmbH) are used. Two different milling times are chosen to determine whether a correlation between the monitored values and the resulting distribution can be detected. Particle breaking is finished at a given time dependent on the specific power input and the course of rotation speed will remain constant. This is proven by analysis of the samples C and D. For sample E a PTFE suspension (Hostafon© TF 5032, Dyneon GmbH) is added to a content of 15 wt.% to study the characteristic of the suspension in the state where it is further processed. Characterisation of the suspensions is done by particle size distribution measurements using a HELOS laser diffraction system (Sympatec GmbH). The received distributions for samples A and B, and C, D and E are depicted in Fig. 1a and b, respectively.

The particle size density distribution of sample A and B shows two maxima at about 3.5 and 7 µm. For the ultrasound treated sample the peak at 3.5 µm diminishes and an additional maximum at 16.5 µm indicates that some of the smaller particles re-agglomerate during the ultrasound treatment. Power ultrasound input is characterised by cavitation events that causes high tensions in the transient bubbles leading to particle breaking. On the other hand the ultrasonic treatment can enlarge particle agglomerates by an enhanced mobility of the solid compounds in the suspension.

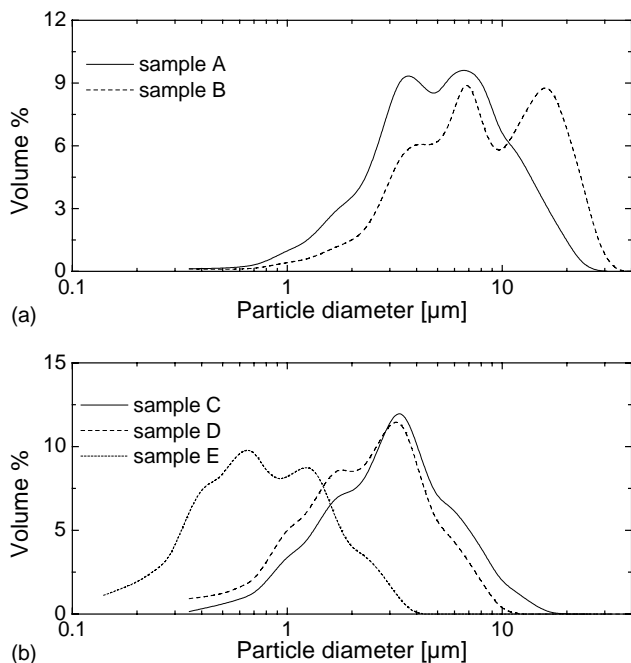


Fig. 1. (a and b) Particle size distribution of carbon suspensions treated by different mixing and milling processes.

The particles of the ball-milled PTFE free samples C and D show a nearly monomodal distribution with a distinct maximum at $3.5 \mu\text{m}$. Larger agglomerates are destroyed efficiently and distribution becomes narrower.

The extended milling duration causes only a slightly continuation of size reduction. This corresponds with the online recorded torque and rotation speed characteristics of the ball-mill which remain nearly constant after ca. 10 min of milling.

The distribution of the PTFE containing sample is characterised by comparatively small particle diameters with two maxima at $0.6 \mu\text{m}$ and between 1 and $2 \mu\text{m}$. This effect can be caused by a steric stabilisation of the disintegrated particles [11]: During the milling, PTFE particles become uniformly distributed and long chain polymeric molecules are adsorbed on the particle surface and hinder the re-agglomeration of the carbon. Another factor of influence is that the PTFE suspension is stabilised by a non-ionic dispersion agent (5 wt.% related to the solid fraction [12]) to prevent aggregation of the PTFE particles itself. This auxiliary material stabilises the disintegrated carbon black as well. Further, the particle sizes of the PTFE suspension is part of the measured distribution. According to the product information of the used Hostaflo[®]-suspension [12], PTFE particles are in the size of $0.1\text{--}0.3 \mu\text{m}$, so the shift in the distribution to diameters below $0.4 \mu\text{m}$ can be explained.

Under the aspect of material processing ball-milling improves stability, reduces sedimentation and hence extends processability. The resulting narrow distribution simplifies the further processing by a wet spraying technique and the choice of the right nozzle size and operation parameter. The

feature of an online-control of the relevant process parameters is an important tool for further advances towards a production sequence under industrial boundary conditions. By monitoring the milling parameters a quality control for the suspensions can be established at an early stage of MEA fabrication.

2.2. MEA preparation

All investigated MEAs are prepared with Nafion[®] 117 membranes (DuPont) and 20% Pt/XC-72 for the cathode and 40% PtRu (1:1)/XC-72 for the anode (both catalytic carbons by Heraeus). Ketjenblack[®] EC300-J (Akzo Nobel) is used as carbon for the diffusion layers. For the hydrophobic diffusion layers a PTFE suspension (Hostaflo[®] TF 5032, Dyneon GmbH) is added to a content of 15 wt.%. For the catalytic layers, a 15 wt.% Nafion[®] content is adjusted by addition of an ionomer solution (15 wt.% in lower aliphatic alcohols, DuPont). Backing structure for all electrodes is a carbon cloth (Kynol) with a thickness of ca. 0.44 mm.

Different catalyst/diffusion layer configurations are investigated for a liquid feed DMFC. The first generation of MEA (type A) is made by a diffusion structure as substrate that is coated by spraying an ink containing the catalytic carbon. Formation of the MEA occurs then by hot-pressing the two catalytic coated backings onto a pre-treated Nafion[®] membrane. An alternative fabrication technique is examined by direct coating of the membrane with the catalytic material and combine this three-layer structure with two diffusion backings (type B MEAs). Due to the separated manufacturing of the diffusion structure and the catalytic coated membrane an improved contact between membrane, ionomer and the catalyst is expected after hot-pressing the coated membrane. Thus, a higher efficiency in the use of catalytic material and ionomer is expected. The configuration of the structural layers is shown in Fig. 2.

2.3. Preparation of type A MEAs

Preparation of type A MEAs starts with the fabrication of the diffusion backings. The carbon cloth is cleaned and made partly hydrophobic by spraying a PTFE suspension onto its surface, up to a content of 15 wt.%. Additionally, adherence between the carbon layer and the clothing is improved, to increase mechanical strength. The dried and pre-milled carbon powder is mixed with *i*-propanol and milled in the ball-mill corresponding to sample E in Section 2.1. PTFE suspension is added after 5 min. The resulting suspension can be sprayed easily on the carbon cloth backing, followed by vigorous hand-rolling with a stainless steel cylinder to compress the structure. The carbon loading is adjusted to ca. 8 mg/cm^2 to fill the macroscopic voids of the carbon cloth and assure an uniform micro-porosity in all directions. The backings are finished by sintering for 120 min at $335 \text{ }^\circ\text{C}$.

The catalytic layer is applied by spraying the catalytic ink on the diffusion backing. This is prepared by drying and high

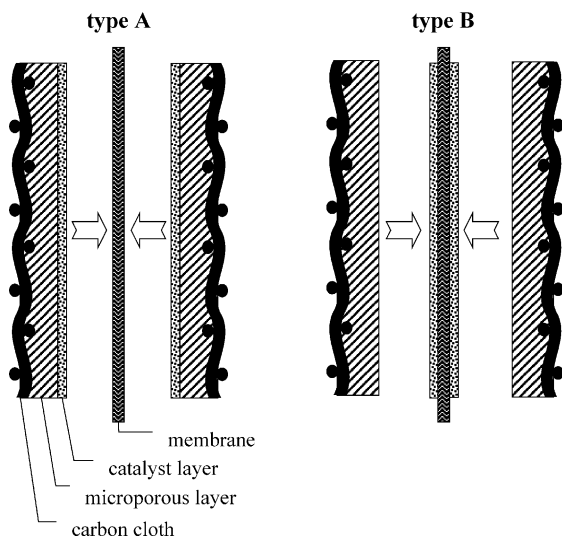


Fig. 2. Configuration of catalyst/diffusion backing and membrane for type A and B MEAs.

speed milling the catalytic carbon followed by mixing with ionomer solution, water and *i*-propanol in an ultrasound bath for 15 min. The resulting slurry is sprayed onto the diffusion layer up to a loading of $1 \text{ mg}_{\text{Pt}}/\text{cm}^2$ for each electrode and dried at 60°C in a convection oven. To improve the interface contact between the catalytic coated backing and the membrane a thin layer of ionomer-solution is sprayed on the electrode surface. Resulting electrodes are ca. 0.7 mm thick with a catalytic layer thickness of ca. $40 \mu\text{m}$. The MEA is assembled by hot-pressing the catalytic coated backings on a pre-treated Nafion[®] membrane under a specific load of 10 MPa for 3 min at 135°C .

2.4. Preparation of type B MEAs

The diffusion layers and the catalytic ink for the type B MEAs are produced according to Section 2.3. In contrast, the catalytic ink is now sprayed directly onto the membrane. The layer is bonded and fixed by hot-pressing at 135°C under a load of 10 MPa for 3 min. This results in a layer thickness of $50\text{--}60 \mu\text{m}$ for the $1 \text{ mg}_{\text{Pt}}/\text{cm}^2$ loading. The catalytic coated membrane is combined with two diffusion backings, prepared as described previously, to complete the MEA.

3. Results and discussion

All MEAs are characterised in a test station with a single cell consisting of two graphite plates with heated stainless steel endplates. Fourteen parallel, 1 mm deep channels with a width of 2 mm are machined into the graphite plate to form the flow field. MEAs are mounted in the cell and re-hydrated by rinsing the anode compartment with 0.75 M methanol. All measurements, if not otherwise mentioned, are recorded

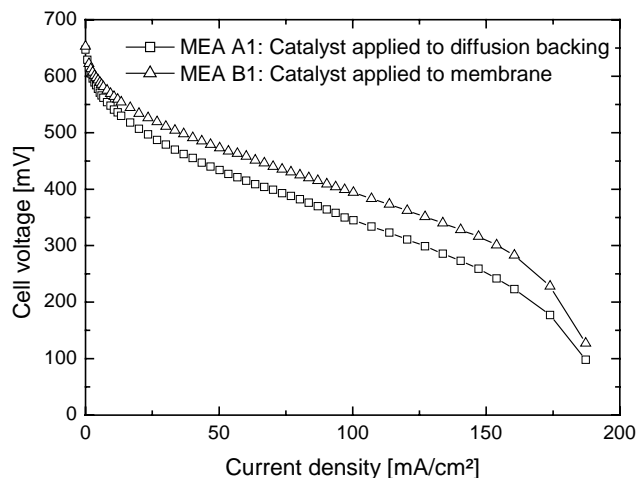


Fig. 3. Polarisation curves for MEA A1 (catalyst loading anode/cathode = $1/1 \text{ mg}_{\text{Pt}}/\text{cm}^2$) and MEA B1 (catalyst loading anode/cathode = $1/1 \text{ mg}_{\text{Pt}}/\text{cm}^2$). Conditions: $T_{\text{cell}} = 80^\circ\text{C}$, $c_{\text{MeOH}} = 0.75 \text{ M}$, O_2 -operation, cathode/anode overpressure = 0.1/0 bar.

at anode flow rates of $5 \text{ cm}^3/\text{min}$. The oxygen flow rate is adjusted to $350 \text{ cm}^3/\text{min}$.

3.1. MEAs of type A and B—influence of catalytic layer configuration

Fig. 3 depicts the polarisation characteristic for the type A and B MEAs. MEA B1 shows a superior characteristic over the complete current density range due to a more efficient degree of utilisation of catalytic material. Applying the catalytic layer to the membrane and subsequently hot-pressing results in very uniform layers and excellent contact of catalyst and ionomer with the proton conducting membrane. Adherence is improved and the extension of the ionomer network increases by embedding of catalytic carbon into the membrane [10,13]. Additionally, the loss of catalytic active sites by incorporation of particles into the porous diffusion layer is prevented by this preparation method. This is affirmed by the somewhat higher catalytic layer thickness for the catalyst coated membrane.

To confirm these assumptions MEA B2 is prepared with half the loading of noble metal ($0.5 \text{ mg}_{\text{Pt}}/\text{cm}^2$) for both, anode and cathode. Thus, catalytic layer thickness' is reduced to $30 \mu\text{m}$. The received polarisation curve is shown in Fig. 4 compared to MEA B1.

Although the catalytic amount is reduced to the half the performance of MEA B2 is for the low- and mid-current range quiet equal to the higher loaded MEA. This is in good agreement with the pre-mentioned increase in utilisation of catalytic material, ionomer and literature [14].

The diffusion limited performance at current densities beyond $160 \text{ mA}/\text{cm}^2$ for MEAs A1 and B1 becomes less distinctive, resulting in higher limiting current densities. Besides the higher catalyst utilisation the thinner catalytic layer enhances mass transfer to and from the three phase

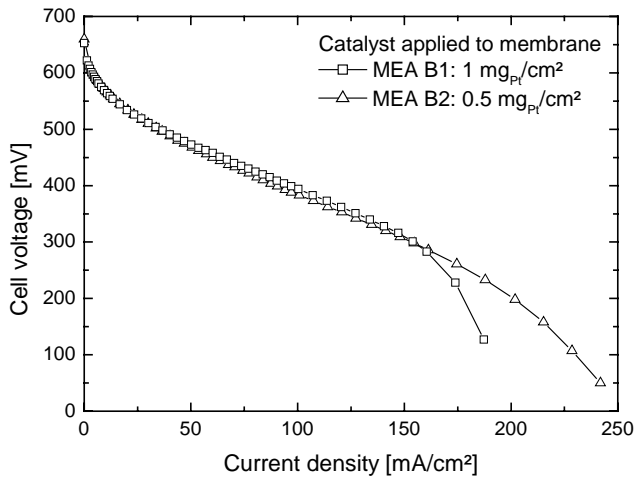


Fig. 4. Polarisation curves for MEA B1 (catalyst loading anode/cathode = 1/1 mg_{Pt}/cm²) and MEA B2 (catalyst loading anode/cathode = 0.5/0.5 mg_{Pt}/cm²). Conditions: $T_{\text{cell}} = 80\text{ }^{\circ}\text{C}$, $c_{\text{MeOH}} = 0.75\text{ M}$, O₂-operation, cathode/anode overpressure = 0.1/0 bar.

boundary inside the catalytic layer. The better supply with educt as well as the advanced removal of CO₂ from the anode, respectively, water from the cathode out of the reaction zone reduces potential losses. At high current densities large amounts of gaseous methanol and CO₂ appear in the anode outlet flow, coming from the active sites. By this a blocking of parts of the porous layers occurs resulting in a lower efficiency of catalyst utilisation. The same effect is notable for the cathode side. Water, coming from the anode and generated on the cathode causes a flooding of pores and hinders the reactants to reach the active sites. By a decrease in layer thickness transport limitations are minimised by a shorter length of diffusion paths.

3.2. MEAs of type C—*influence of layer thickness and gas/liquid management*

For a further increase in mass transfer a reduction of layer thickness has to occur. For type C MEAs the diffusion layer is therefore prepared by applying the carbon ink on the catalytic coated and hot-pressed membrane instead of the carbon cloth, forming a five-layer structure (Fig. 5). Thus, the resulting thickness of the porous layer is adjustable over a wide range because the filling of the carbon cloth voids for an uniform distribution of reactants in- and through-plane is no longer precondition. The final structure is hot-pressed again and the macroporous carbon cloth is attached between the diffusion structure and the graphite housing of the cell to ensure sufficient electrical conductance and mechanical support.

Two different MEAs are fabricated with different composition of the anodic diffusion layer. MEA C1 is prepared using a catalytic coated membrane (0.5 mg_{Pt}/cm²) with an additional layer of carbon/PTFE as cathodic and anodic diffusion structures. MEA C2 is fabricated similar, except for

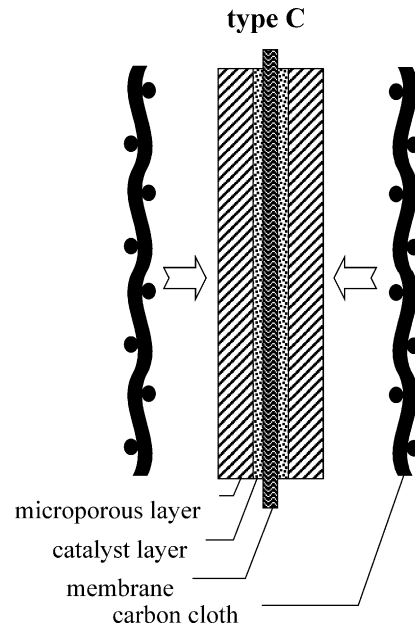


Fig. 5. Configuration of catalyst/diffusion backing and membrane for type C MEAs.

the anode PTFE is replaced by the respective amount of Nafion®-ionomer. Therefore, the anodic diffusion layer becomes more hydrophilic to facilitate methanol mass transport. On the other hand, the removal of CO₂ may be affected by the lower fraction of hydrophobic pore volume for gas transport. The microporous layer loading is reduced to 3.5 mg/cm² for both electrodes, layer thickness is 0.11 mm. For both MEAs a sintering step did not occur due to the glass transition temperature of Nafion® of ~150 °C. Fig. 6 shows the current-voltage characteristics for MEA C1 compared to MEA C2.

MEA C2 with the more hydrophilic anode structure shows further improved performance at high current densities. The

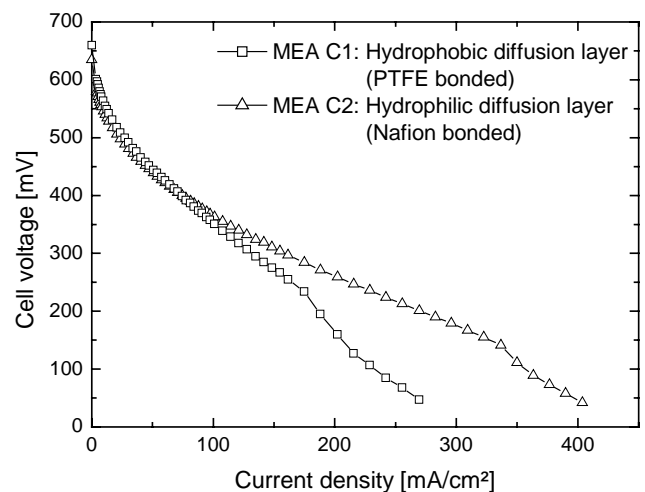


Fig. 6. Polarisation curves for MEA C1 and MEA C2 (both: catalyst loading anode/cathode = 0.5/0.5 mg_{Pt}/cm²). Conditions: $T_{\text{cell}} = 80\text{ }^{\circ}\text{C}$, $c_{\text{MeOH}} = 0.75\text{ M}$, O₂-operation, cathode/anode overpressure = 0.1/0 bar.

MEA with the more hydrophobic anodic diffusion layer yields similar values for low currents and flattens at current densities beyond 100 mA/cm^2 . Nevertheless, both curves are still characterised by distinct potential losses for higher current operation due to mass transport limitations. For a current density of 0.4 A/cm^2 a theoretical CO_2 production rate of about $1 \text{ cm}^3 \text{ CO}_2/\text{cm}^2 \text{ min}$ results, showing the importance of efficient gas removal from the cell. Gas phase and the liquid phase methanol moves in opposite directions. Gas has to be released from the structural MEA layers to the flow field and to the cell outlet. The type of flow observed in the flow channels of the cell ranges from finely dispersed bubbles to large slugs of gas and annular flow [15].

The hydrophobic character of the PTFE bonded diffusion layer limits methanol supply for MEA C1 at increased current densities. In contrast, the more hydrophilic structure used for MEA C2 improves transport of liquid phase methanol but leads to potential losses for current densities beyond 340 mA/cm^2 due to the excessive CO_2 formation. Thus, effective area is reduced by blocked pore structures and gas slugs in the flow channels.

Measurements with ten times increased methanol flow rate are made to estimate the significance of convective CO_2 removal. To diminish the influence of a better methanol transfer caused by the higher flow rate, MEA performance under high flow in comparison to an increased methanol concentration of 2 M is shown in Fig. 7.

The increased methanol flow rate causes an enhanced MEA-performance in higher conversion rate operation. The CO_2 is removed better out of the layers and the flow field channels by the high volumetric flow. In comparison the higher methanol concentration results only in the region between 90 and 140 mA/cm^2 in an enhanced performance. For lower current densities the higher methanol concentration on the anodic boundary of the membrane results in higher methanol crossover and therefore reduced cell voltage. In

the mid-current range the better supply with educt prevails the negative effects. For high conversion rates the electrode morphology inhibits a fast removal of CO_2 . The transport limitation in the region of bubble formation compensates the higher availability of methanol, showing the strong influence of layer structure, arrangement and operation conditions on the removal of CO_2 and thus on overall MEA performance.

3.3. Influence of sintering step

Sintering of the backing results in partially melting and thus a flow of PTFE and a more uniform distribution. Due to the non-sintered state of the used diffusion layers for MEA C1 the formation of a widespread hydrophobic pore-network may not be suited for an sufficient liquid-management. Fig. 8 shows SEM-images of PTFE bonded backings without (Fig. 8a) and with (Fig. 8b) an additional sintering step.

The formation of the net of thin fibres in Fig. 7b is due to the PTFE contained in the diffusion backing. These hydrophobic structures are obtained only for the rolled and sintered backing. These fibres are observed in other work, mostly when a rolling process is affiliated [16–19]. However, polarisation characteristics of MEAs with non-sintered and sintered diffusion backings show a massive increase in high current density performance for the latter one (Fig. 9). MEA configuration is according to type B but diffusion backings are made with a thinner carbon cloth (*Tenax*, thickness 0.33 mm) and a reduced loading of 5 mg/cm^2 to further advance mass transport and reduce ohmic losses. In addition to the measurements at moderate conditions, polarisation curves for increased cell temperature, pressure and methanol concentration are diagrammed.

The obvious increase in performance for the MEA with sintered backings supports the mentioned assumption on the beneficial influence of the thermal treatment on the formation of a hydrophobic network for efficient gas management. For the thin PTFE-bonded and sintered backings the interaction of layer thickness, hydrophilic regions for the supply with methanol and hydrophobic spheres for gas transport is adjusted satisfactory. Even at the considerable current densities under elevated operation conditions the sintered MEA features good and stable performance without a collapsing of cell voltage at high CO_2 production rates.

The investigations show the importance of an efficient adjustment of the structural layers to receive powerful MEAs. Improved characteristics are obtained when mass-transfer limitations especially on the anode can be reduced by the use of thinner diffusion backings and a definitely adjusted ratio of hydrophobic and hydrophilic spheres inside the porous structure. This can be achieved by variation of the binder material or alternatively by an additional thermal treatment at temperatures beyond the melting point of the PTFE. Hydrophobic and sintered backings shows the best mass transfer properties even at critical operating conditions. A preparation strategy of hard-wearing catalytic coated membrane could be established and the platinum load could be halved

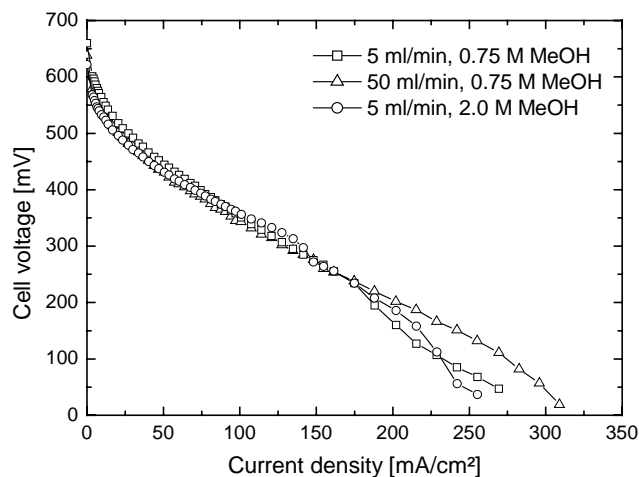


Fig. 7. Polarisation curves for MEA C1 (catalyst loading anode/cathode = $0.5/0.5 \text{ mgPt/cm}^2$). Conditions: $T_{\text{cell}} = 80^\circ \text{C}$, $c_{\text{MeOH}} = 0.75 \text{ M}/2 \text{ M}$, O_2 -operation, cathode/anode overpressure = $0.1/0 \text{ bar}$.

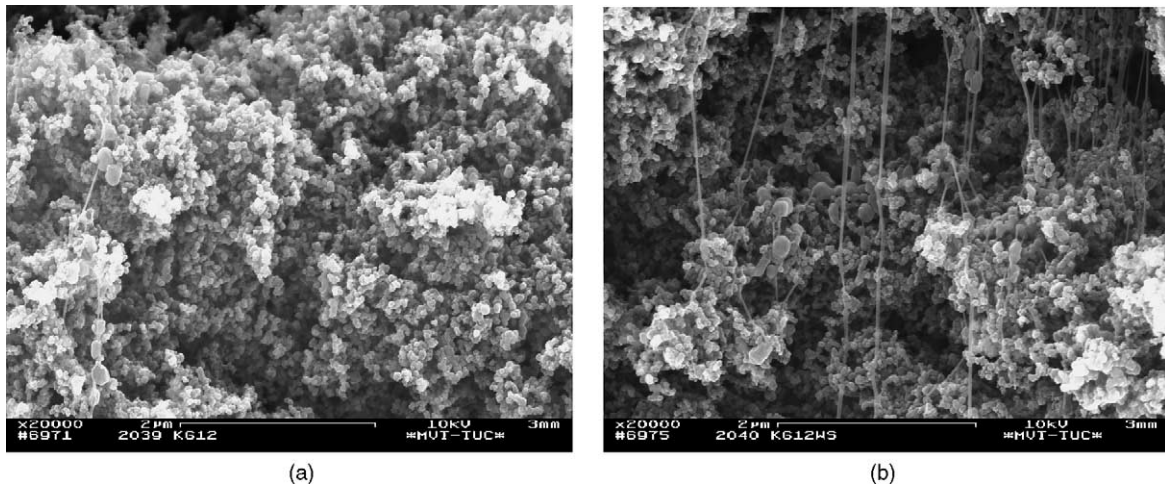


Fig. 8. SEM images of PTFE-bonded non-sintered and sintered diffusion backings, Ketjenblack EC300-J with 15 wt.% PTFE: (a) rolled and (b) rolled/sintered for 120 min at 335 °C.

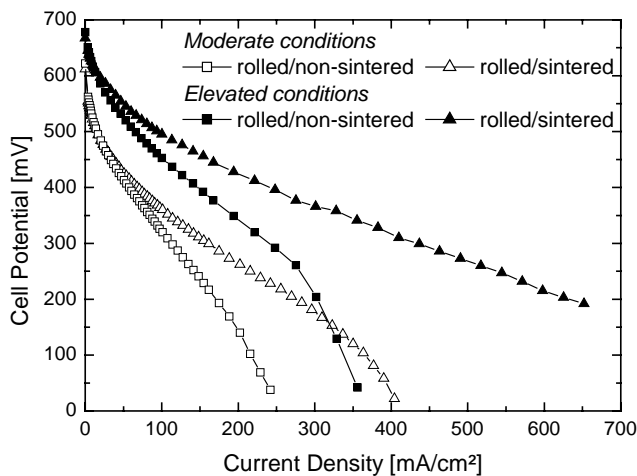


Fig. 9. Polarisation curves for MEAs with rolled/sintered and rolled/non-sintered diffusion backings (both: catalyst loading anode/cathode = 0.5/0.5 mg_{Pt}/cm²). Moderate conditions: $T_{\text{cell}} = 80\text{ }^{\circ}\text{C}$, $c_{\text{MeOH}} = 0.75\text{ M}$, O₂-operation, cathode/anode overpressure = 0.1/0 bar. Elevated conditions: $T_{\text{cell}} = 115\text{ }^{\circ}\text{C}$, $c_{\text{MeOH}} = 2\text{ M}$, O₂-operation, cathode/anode overpressure = 4.5/2.5 bar.

to 0.5 mg/cm² at nearly the same performance by the better utilisation of the applied material. The measured polarisation curves are satisfactory under consideration of the low material cost for the necessary amount of precious metal components.

4. Conclusions

Preliminary investigations concerning the influence of suspension preparation on particle size distribution of the diffusion layer carbon show reduced and narrower particle sizes for the ball-milled samples, simplifying the further processing. The status of the particle breaking can be mon-

itored online by recording the torque and rotation speed course of the ball-mill. The resulting suspensions are long time stable and can be processed and sprayed easily by an airbrush gun.

Different application techniques for the catalytic layers are investigated. Depending on the structural arrangement a distinctive increase in cell performance is obtained. Best results are achieved when the catalytic carbon is applied to the membrane. This is due to an increase in catalyst efficiency and a superior formation of the proton conducting ionomer network.

In analogy to the catalytic coating of the membrane the diffusion layer suspension is sprayed alternatively to the previous prepared catalyst coated membrane. This leads to an uniform diffusion structure even at low loading. By use of hydrophobic carbon suspensions only small improvement concerning limiting current and power density is notable, due to the absence of a sintering step. In relation to the carbon cloth based diffusion layers in combination with catalytic coated membranes even a deterioration of performance is attained.

Besides the PTFE bonded, hydrophobic anodic diffusion layer a hydrophilic modification with Nafion® ionomer as binder is evaluated and an increase in performance is received. The better mass transport facilities of the MEA affects higher limiting current and power densities of about 55 mW/cm² at a current density of 255 mA/cm². On the other hand, the hydrophilic nature of the Nafion® bonded electrode impedes efficient CO₂ removal at high current densities. MEAs produced with carbon cloth bonded diffusion backings and a reduced thickness including a thermal treatment of the PTFE show an improved performance and better gas and liquid phase management.

Further work concerning the preparation influence on MEA performance will follow. This has to occur under particular observation of gas evolution and removal on the anode side. For a successful operation at high current

densities and temperatures a fast and entire removal of CO₂ is indispensable.

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