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ORIGINAL PAPER

Pseudo-half-cell measurements on symmetrical catalyst-coated membranes and their relevance for optimizing DMFC anodes

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Abstract The preparation of catalyst-coated membranes (CCMs) with two anodic catalyst layers (60% PtRu/C as catalyst) using a decal technique and their characterization by pseudo-half-cell measurements using both sides of the CCMs by simply turning the test cell around, allows the characterization of quasi-identical CCMs with a much smaller experimental uncertainty than observed for the classical direct methanol fuel cell (DMFC) testing of membrane electrode assemblies under similar working conditions (5 mV vs. 12 mV at a current density of 140 mA cm^{-2}). With this new sensitive tool, we study the influence of the dispersing technology and the Nafion content on the performance of DMFC anodes. While the ionomer content shows a broad optimum between 20 and 40%, the dispersing technology does not have a strong impact on the fuel cell performance under the experimental conditions of this study, but influences strongly the stability of the catalyst slurries and the homogeneity of the electrode coatings.

Keywords Anode · Catalyst layer · Decal technique · Direct methanol fuel cell · Membrane electrode assemblies · Pseudo-half-cell measurement

1 Introduction

One important step on the pathway to successfully commercializing direct methanol fuel cell (DMFC) systems of the watt to kilowatt class (e.g. replacing lithium-ion batteries in portable applications or lead-acid batteries in small forklift trucks) is the development of membrane electrode assemblies (MEAs) with excellent electrochemical performance and durability producible in continuous processes. As a consequence, research must be carried out on optimizing the composition and microstructure of catalyst layers on a laboratory scale, as well as in terms of their reproducible homogeneous fabrication. At Forschungszentrum Jülich, gas diffusion electrodes (GDEs) for the MEAs needed to equip 100-cell DMFC stacks are already fabricated with an automated coating machine.

Due to the fact that MEAs are quite complex entities composed of different functional layers, in order to specifically study and improve the properties of an individual layer, the effects of the other components must be limited as far as possible. Accordingly, we developed a novel combination of the preparation of catalyst-coated membranes (CCMs) with two identical ‘anodic’ electrodes prepared simultaneously using a decal technique (see below) and their characterization in pseudo-half-cell measurements using fine platinum nets as diffusion substrates instead of classical carbon materials (cloth or non-woven, with or without microlayer). With this experimental approach, we studied the effect of the Nafion content in the anodic catalyst layer, as well as the influence of the dispersing technology used to prepare the catalyst ink on the cell performance. As these symmetrical CCMs were prepared with one single coating of catalyst slurry on a decal substrate, we were able to check the reliability of the electrochemical results by alternately using both electrodes as methanol-consuming and hydrogen-producing electrodes, respectively. Different analytical techniques, such as dynamic light scattering, rheology and optical microscopy, were applied to study the properties of the dispersions and the dried electrodes.

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Of course, there is some concern as to whether results obtained with such symmetrical CCMs can be directly transferred to the optimization of DMFC anodes for complete MEAs. In general, MEAs are prepared by a coating and subsequent hot-pressing step in three fundamentally different ways: (i) by directly coating a membrane with a catalyst ('CCM method') followed by the addition of the gas diffusion layer (GDL), (ii) by depositing the catalyst layer on the GDL and subsequently laminating the gas diffusion electrode (GDE) on the membrane ('GDE route') and (iii) by the 'decal' technique, i.e. first preparing the catalyst layer on an inert substrate and then transferring it to the membrane; the GDL is then added in a final step. From the broad body of literature concerning comparative studies on preparation methods of MEAs for DMFCs, no clear trend was discerned in terms of which of these techniques (and variants thereof) might be the most favourable, although several studies claim the CCM technique to be advantageous (see below). It appears that some preparation steps such as the careful adjustment of the composition of the catalyst ink, the choice of coating technology (e.g. brushing, bar coating, screen printing) or the parameters of the hot-pressing step, could be more important for the overall fuel cell performance than the decision between using the CCM, GDE or decal strategy (cf. e.g. [1–4]). Nevertheless, the MEA preparation route can have significant effects on the macro- and microstructure and thus on the transport properties of the catalyst layers [3, 5–8] as well as on the electrocatalytic activity [2, 7–10]. Although different macroscopic structures of catalyst layers with the same composition produced by coating different substrates (onto decal sheets, gas diffusion layers or directly onto membranes) can result in enormous differences in fuel cell performances, especially in the so-called 'mass-transport region' [2, 3, 5, 6, 9, 10], their influence at higher cell voltages has often been reported to be rather small (cf. [3, 5–7] and Fig. 4a in [8]). As a consequence, we expect the results of our study to be relevant for the optimization of MEAs prepared by all three assembling routes, as long as the technically relevant performance at high cell voltages (and thus high electrical efficiencies) is considered. As part of this work, we explicitly checked whether this was the case for MEAs in which the anodes were prepared by a decal step and joined with cathodic GDEs. Investigations must be performed separately to verify whether the results presented in the following are also applicable for the production of anodes as gas diffusion electrodes.

Very few systematic studies have looked at the influence that different techniques used for ink formulation have or that the change between wet and dry coating procedures has on the properties of the mircoporous [9] and catalyst layers [7]. The effect of the ionomer content in the anode on the DMFC performance of MEAs has already been studied by many research groups. Depending on the catalyst material used (PtRu black or supported on carbon in different loadings), these papers give very different optimal Nafion loadings in weight percent [7, 11–16].

2 Experimental

2.1 Preparation of symmetrical CCMs and classical MEAs

To manufacture symmetrical CCMs with two quasi-identical anodic catalyst layers, commercial DMFC anode catalyst powder (60% PtRu/C, HiSPEC 10000, Johnson Matthey Fuel Cells Ltd.) and various amounts of ionomer solution (15% Nafion 1100 EW in a mixture of water and isopropanol, IonPower Inc.) were dispersed in appropriate mixtures of water, 1-propanol and isopropanol in total volumes of 1–3 mL in cylindrical glass containers. Three different techniques were employed: (i) the use of a magnetic stirrer (Variomag® Poly 15) for 24 h with 600 revolutions per minute (stirring power <10 W), (ii) the use of a high shear mixer (Ultra Turrax T8, IKA Labortechnik GmbH) for 2 min at 10,500 r.p.m. (output ~50 W), and (iii) agitating the mixture for 2 min in an ultrasonic homogenizer (Bandelin HD 2200 at 15% of its nominal power with alternating intervals of 0.4 s ultrasound and 0.6 s idle time, ~15 W mean HF output). The catalyst inks prepared using one of these three processes were coated on an inert decal substrate (PTFE-coated glass-fibre fabric Thomaplast®/Thomafluor NRN, purchased from Reichelt Chemietechnik GmbH & Co) in predefined forms by automated bar coating (Coatmaster 509 MCI, Erichsen GmbH & Co. KG, used with a coating speed of 5 mm/s and gap clearances between 160 and 420 μm) and dried slowly. Afterwards, two of these 'anodes' were transferred to the opposite sides of a Nafion® 117 membrane (DuPont) by a hot-pressing step at 130 °C. The transfer rate was between 95 and 100% for all cases discussed in the following. The complete CCM preparation technique is further illustrated in Fig. 1; more experimental details are given in the corresponding caption. To obtain a nearly constant catalyst loading of about 2 mg cm^{-2} per electrode for all samples discussed in the following, polymer films with different thicknesses were used as masks during the coating process. Nevertheless, the catalyst loading of the samples in this study varied between 1.8 and 2.5 mg cm^{-2}, which may of course have some influence on the data discussed hereafter.

For DMFC performance tests with full size MEAs, 'decal' anodes prepared as described above were first hot-pressed onto a Nafion 117 membrane and then joined with anodic

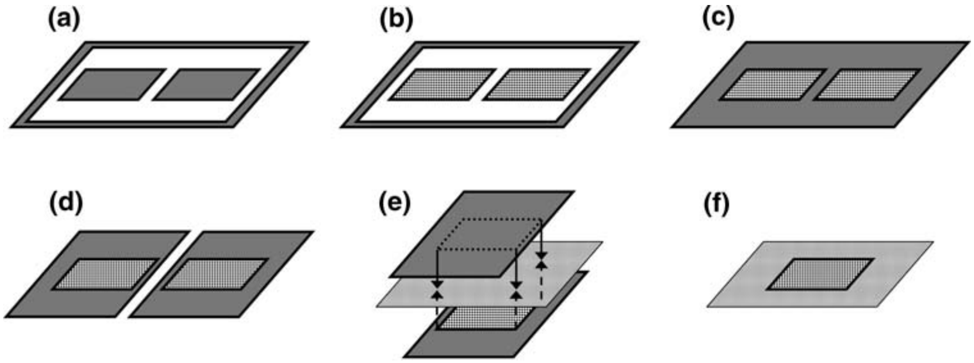

Fig. 1 Manufacturing technique for CCMs: **a** laminating a polymer mask onto a decal substrate, **b** filling the holes with catalyst ink by bar coating, **c** delaminating the polymer film after 24 h of slow drying at RT in an atmosphere almost saturated with solvent under an upsidedown Petri dish, followed by drying at 60 °C in an oven, **d**, **e** cutting the substrate and hot-pressing two quasi-identical electrodes onto opposite sides of a Nafion 117 membrane to obtain **f** a catalyst-coated membrane

GDLs (carbon cloth with microporous layer, manufactured in Jülich) and cathodic gas diffusion electrodes (produced in Jülich, 2.0 mg Pt cm^{-2}, 60% Pt/C HiSPEC 9100 from Johnson Matthey as catalyst, woven GDL with microporous layer) in a second hot-pressing step.

2.2 Physicochemical characterization

The rheological behaviour of catalyst inks was measured with a rotational rheometer in plate-plate geometry (Rheo Stress 1, Haake). To assure good processability of the catalyst inks, their viscosities at a shear rate of 50 s^{-1} were adjusted to values between 50 and 400 mPa s by adding different amounts of solvents. This shear rate is close to the conditions during the bar coating of the catalyst inks onto the decal substrate.

The particle size distribution in diluted catalyst slurries was studied by photon cross-correlation spectroscopy (PCCS; Nanophox, Sympatec GmbH). Although this special dynamic light-scattering technique involves the use of two laser beams, which allows the characterization of turbid and opaque dispersions in principle, the catalyst inks had to be diluted with the same mixture of water and alcohol used for their preparation until the solid content was below 0.1% by volume. Each sample was characterized by 10 measurements (of 50 min each) performed in a row to gain information about agglomeration and/or sedimentation processes. Rough estimations of the particle size distributions were deduced from the individual cross-correlation functions by means of a non-negative least squares fit assuming spherical particles.

Optical microscopy was used to characterize the dried electrodes on the ‘decal’ substrates. The fraction of cracks within the catalyst layers was calculated from high contrast images of digital photos in which areas covered with catalyst appeared black, while regions of the substrate not covered appeared white.

2.3 Pseudo-half-cell measurements on symmetrical CCMs

While the use of reference electrodes for the separation of the effects of anode and cathode in DMFCs is a very challenging technique [17–19], pseudo-half-cell measurements represent a much simpler and more valuable approach for gaining information on the electrochemical properties of single electrodes in CCMs or MEAs [20]. The general set-up used in this study is depicted in Fig. 2. CCMs together with fine platinum nets as diffusion layers and current collectors were characterized with a hydrogen-producing cathode at 80 °C with 1 M aqueous methanol solution as the anode feed. Prior to the measurements, the cathode was flushed with nitrogen. Hydrogen was then produced at a small current density for 5 min. Afterwards, the anode polarization curves were measured up to a cell voltage of 450 mV. We assumed that the cathode reaction at the PtRu/C catalyst, i.e. the reduction of hydrogen ions transported through the membrane, to be not much more, if at all, polarizable than the same reaction at a platinum electrode, which is normally used as the counter electrode in pseudo-half-cell experiments [21]. The ohmic resistances of the CCMs were deduced from the high-frequency intercepts of the corresponding Nyquist plots with the real axis of the cell impedances which were measured with an IM6 electrochemical workstation (Zahner GmbH, Kronach, Germany). Nevertheless, all anode polarization data presented and discussed in the following has not been *iR* corrected.

2.4 Fuel cell characterization of complete MEAs

To verify the relevance of the results obtained characterizing CCMs with two anodic catalyst layers by pseudo-half-cell measurements for the optimization of DMFC anodes, complete MEAs ($A = 17.6$ cm^2) with decal anodes were

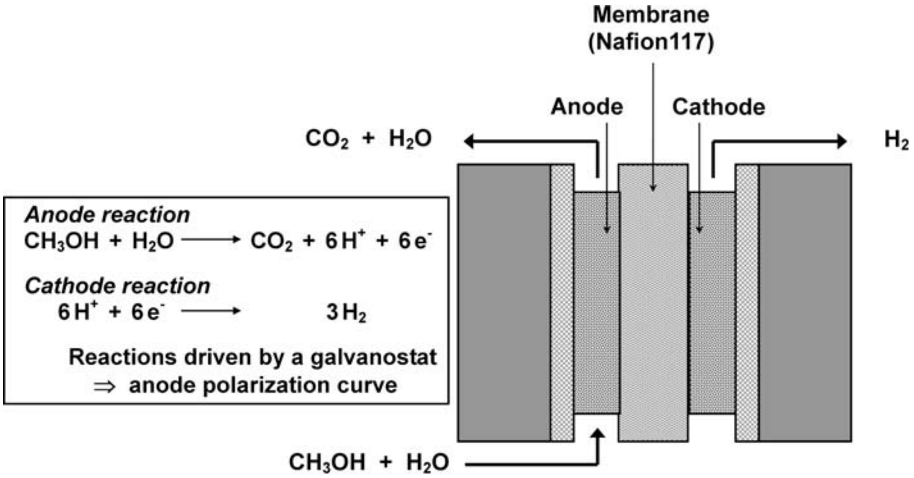

Fig. 2 Scheme of the pseudo-half-cell measurement

mounted in a test cell with graphite flow fields of grid design (1:1:1 mm) and stainless steel endplates equipped with heating cartridges. Polarization curves were recorded at a temperature of 70 °C under ambient pressure using 1 M aqueous methanol solution and air as reactants with rather high constant flows (anode: 0.021 ml cm^{-2} min^{-1} and cathode: 37 ml cm^{-1} min^{-1} corresponding to $\lambda_A \sim \lambda_C \sim 4$ at $j = 500$ mA cm^{-2}).

3 Results and discussion

3.1 Experimental uncertainty of pseudo-half-cell measurements performed on quasi-identical symmetrical CCMs

Our experimental approach using a catalyst-coated membrane with two quasi-identical anodic catalyst layers enabled us to study the reproducibility of electrode fabrication and half-cell measurements by simply turning the test cell around. Several current–voltage curves were measured in a row to obtain constant values for the anode polarization under load. For nearly all samples, the cell voltages measured at $j = 140$ mA cm^{-2} in the last three of these curves differed by less than 0.5 mV from their average value used in the following. The differences between the anode potentials of the two opposite sides of one CCM at $j = 140$ mA cm^{-2} were generally less than 10 mV (Fig. 3). With a value as small as 2 mV and a standard deviation of 4 mV, the arithmetic mean of the cell voltage after turning the cell around was observed to be neither significantly higher nor lower than in the initial configuration (Fig. 3).

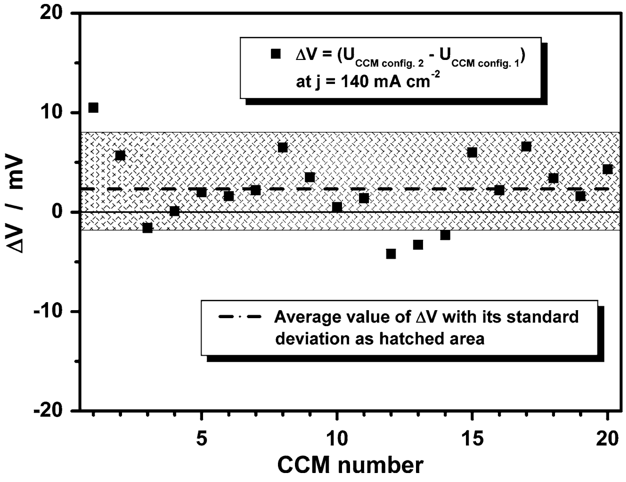

Fig. 3 Differences between the cell voltages at a current density of $j = 140$ mA cm^{-2} measured by pseudo-half-cell measurements at $T = 80$ °C for the opposite sides of CCMs with two quasi-identical 'anodic' electrodes (20 individual samples; config 1: initial configuration, config 2: after turning the cell around)

Variations due to the manufacturing process of several independent CCMs with the same nominal composition added slightly to the experimental error. Although differences between the cell voltages of three quasi-identical CCMs measured at $j = 140$ mA cm^{-2} reached 22 mV in one single case, the standard deviation from the respective mean value was only 5 mV (c.f. Sect. 3.4) for all data presented in the following.

3.2 Influence of the dispersing technology and the ionomer content on the preparation and stability of catalyst inks

The amount of solvent needed to achieve a suitable viscosity of the catalyst inks for the bar-coating process depended heavily on the choice of dispersing technology used and the Nafion content of the ink. As a consequence, different gap clearances were required to produce electrodes with a catalyst loading close to 2 mg cm^{-2}. Under the experimental conditions chosen for this study, the amount of solvent that had to be added to the mixture of catalyst and Nafion dispersion was greater by 50% for inks prepared by ultrasonic agitation than for those fabricated by high shear mixing. This feature, which has already been observed with other catalysts [22], indicates that ultrasonication—despite the smaller nominal energy output—led to a more efficient catalyst dispersion than mechanical agitation by high shear mixing (cf. [23]). While the viscosities of slurries produced with the magnetic stirrer (lowest energy input of the three dispersing tools) were very low within the first minutes compared to those prepared by the two alternative techniques (this short time was all that was required to finalize the ink formulation), within the dispersing time of 24 h chosen for the magnetic stirrer, they thickened remarkably. As a consequence, these slurries needed the highest amount of additional solvent. In terms of the variation of the Nafion content in the dried catalyst layer, it was observed that the slurries with the lowest Nafion proportions required the least solvent. With the exception of one ink composition, no pronounced time-dependent changes were detected in the viscoelastic properties of the slurries during rheological-controlled shear rate tests. In the case of an ink containing only 10% Nafion, the measurements reproducibly indicated rheopectic behaviour. However, this finding could at least partly be explained by the fact that with this particular slurry composition, some instability of the samples was observed during the measurements as a result of sedimentation of the catalyst (see below) and/or loss of solvent due to evaporation.

Dynamic light scattering (after the necessary dilution of the samples) was used to gain information on the stability of the different catalyst inks, as well as to get a rough estimate of the particle sizes. While the choice of the solvent is assumed to primarily determine the minimal particle size being achievable in the dispersion, the dispersing technique and the associated energy input affect the extent to which this minimal size is achieved. It was already obvious by visual inspection that among the three slurries containing 20% Nafion prepared with the three dispersing techniques, the slurry prepared with the magnetic stirrer showed a pronounced sedimentation of material to the bottom of the flask within a few hours. This finding was corroborated by PCCS experiments. From the data shown in Fig. 4a, it is obvious that from the beginning, large particles with diameters greater than 10 µm were present (peak at lag times >100 ms of the correlation curves). The fact that the amplitude of the PCCS curves increased strongly within the timeframe of the experiment (8 h) indicates that sedimentation occurred. As the onset of the curvature at small lag times (below 1 ms in Fig. 4a) proves that also a considerable amount of very small particles is present, the particle size distribution in the dispersion is found to be extraordinarily broad. This can be attributed to the small energy input associated with the use of the mechanical stirrer [22]. In contrast, due to the much higher energy input catalyst inks prepared with the high shear mixer (Fig. 4b) gave rise to slurries with almost exclusively small particles of mainly 300–600 nm in diameter (computed by the Nanophox software, particles assumed to be of ideal spherical shape, particle size distribution not shown here). This does not correspond to individual primary carbon particles but to their so-called aggregate structure [24]. However, these samples also showed some

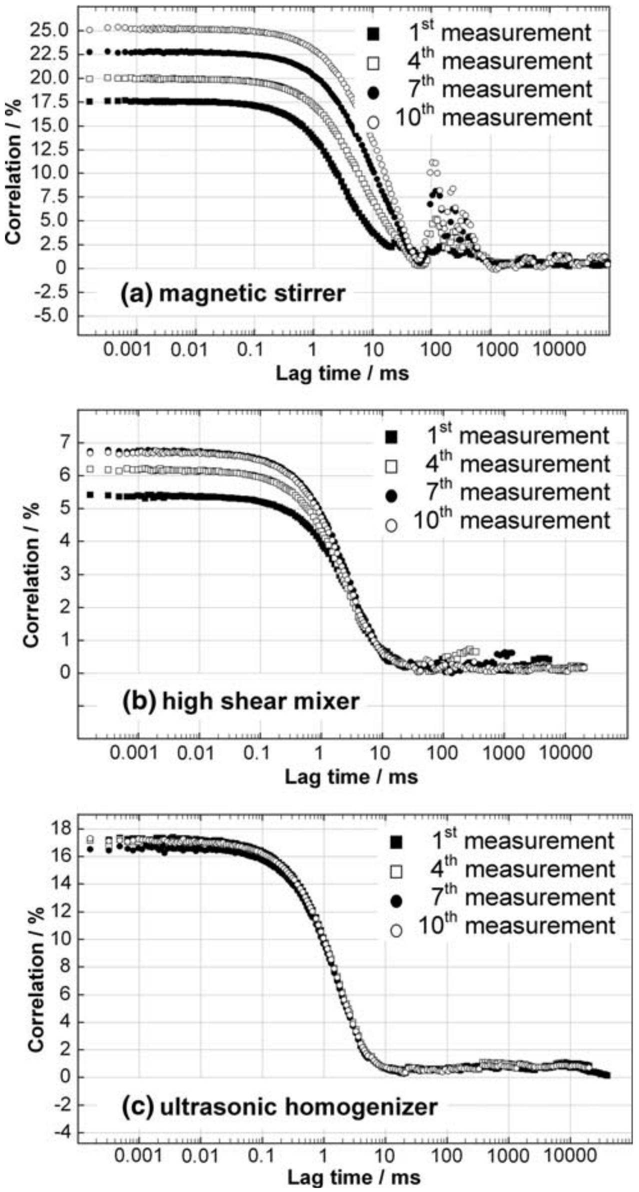

Fig. 4 Photon cross-correlation curves of catalyst inks with 20% Nafion solids content (referred to the total weight of the dried electrodes prepared from these slurries) prepared with **a** a magnetic stirrer, **b** a high shear mixer and **c** an ultrasonic homogenizer

sedimentation, which was not visually obvious but was detected by the PCCS measurement. Dispersing the catalyst and the ionomer in the solvents by ultrasonic homogenization resulted in slurries with a constant particle size distribution (again ~500 nm in diameter) free of large agglomerates for the whole timeframe of the experiment (Fig. 4c). As it has already been described elsewhere, this indicates that ultrasonication can produce dispersions/emulsions with the same or lower particle size and increased stability compared to high shear mixing even if the nominal power output is smaller (cf. e.g. [23]).

The stability of catalyst dispersions depended on their ionomer content to a similar extent. While the particles in inks with low weight fractions of Nafion agglomerated and sedimented quickly, slurries with 20% Nafion or more were much more stable within the timeframe of the experiment and contained almost no large agglomerates, even at the end of the measurements (PCCS measurements not shown here). While the particle size distribution could have an influence on the electrochemical activity of the catalyst layers prepared, the stability is important for the automated fabrication of electrodes on a continuous coating machine. Accordingly, from these findings, it is obvious that from a technological point of view (without taking costs into account) the preparation of catalyst dispersions by ultrasonic homogenizing or (with some reservations) high shear mixing should be preferred to the use of a magnetic stirrer, as slurries with smaller particles and a greater stability are obtained. And as long as the electrochemical activity is not strongly influenced (see Sect. 3.4), the Nafion content should be relatively high (30–40% as a good choice). Of course, some stabilizing effect could alternatively be achieved by adding appropriate additives.

3.3 Characterization of catalyst layers

All catalyst layers formed on the decal substrates after the drying step were characterized by clods of catalyst layer (100–500 μm in diameter) separated by cracks of up to 100 μm wide. These cracks formed in the final phase of the drying step at room temperature. While the shape of the clods was found to depend mainly on the dispersing technology used to prepare the catalyst ink, the number of cracks depended strongly on the amount of Nafion within the electrodes (with the same catalyst loading). The anodes prepared by magnetic stirring of the catalyst ink consisted of many comparatively small islands of catalyst with curved borders separated by numerous but small cracks (Fig. 5a). The fraction of cracks with respect to the total electrode area was slightly less than 20% (Table 1). The anodes made from dispersions prepared with the help of a high shear mixer resulted in a similar structure with somewhat larger 'islands' of catalyst layer (Fig. 5b) and the same or a slightly lower fraction of cracks. From Fig. 5a and b, it becomes clear that the surfaces of the catalyst layers were not perfectly flat. In contrast to this, the structure of the electrodes prepared by ultrasonic homogenization of the slurry was very smooth (Fig. 5c). This might be related to the fact that the catalyst ink prepared by ultrasonication was the most stable one with the narrowest particle size distribution [22]. The edges of the individual clods were sharp in all cases. The diameter of the individual clods and the fraction of cracks were observed to vary significantly for samples with the same nominal composition and similar thickness. However, the average fraction of cracks was basically the same as that observed for the other two dispersing technologies.

The total area of cracks in the catalyst layer was found to increase with Nafion content (Table 1). It could be assumed that one important driving force for the formation of clods is the lateral contraction force caused by the de-swelling of the ionomer phase when the last quantities of solvent are evaporated. The higher the Nafion content in the catalyst layer, the stronger these driving forces for the formation of cracks. Another explanation is related to the fact that electrodes with higher Nafion contents must be thicker to obtain a constant catalyst loading of 2 mg cm^{-2} (from 75–80 μm with 10% Nafion up to ~130 μm for the

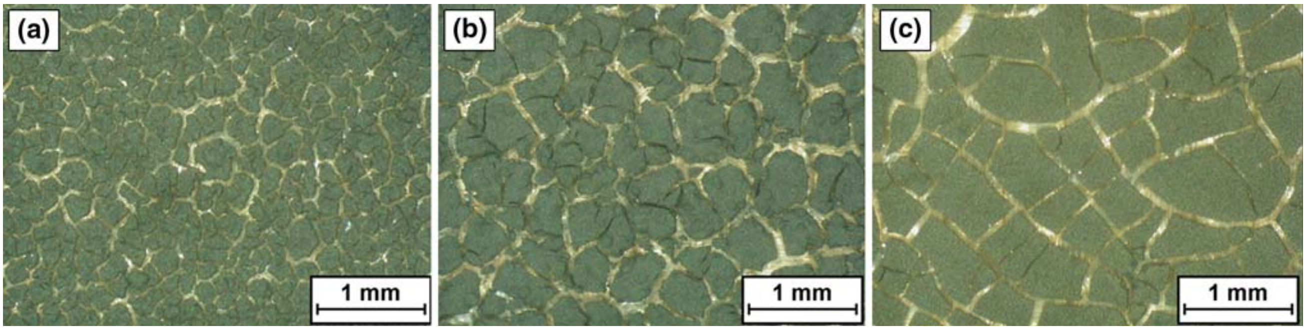

Fig. 5 Influence of the dispersing technology (inks prepared with: **a** magnetic stirrer, **b** high shear mixer, and **c** ultrasonic homogenizer) on the morphologies of dried catalyst layers with the same composition (20% Nafion) on the decal substrate

Table 1 Interdependence between the dispersing technology, the Nafion content and the number of cracks observed in a dried catalyst layer with a precious metal loading of ~ 2 mg cm^{-2} on the decal substrate

Dispersing system	Nafion content/%	Cracks in dry catalyst layer/% of total area
Magnetic stirrer	20	19 (1)
High shear mixer	20	16 (3)
Ultrasonic homogenizer	20	18 (6)
High shear mixer	10	19 (3)
High shear mixer	20	16 (3)
High shear mixer	30	21 (1)
High shear mixer	40	26 (2)
High shear mixer	50	29 (4)

electrodes containing 50% Nafion). From our experience, we know that thicker catalyst layers generally tend to have more cracks than thinner ones with the same composition. After transferring the electrodes to the membrane by hot-pressing, the general trend that the catalyst layers manufactured by magnetic stirring and high shear mixing had much smoother edges than those prepared by ultrasonication of the inks was verified. The back sides of the electrodes were also inspected at this stage and all catalyst clods had flat and even surfaces. Although not analyzed in detail, we observed that the fraction of cracks within the catalyst layers pressed onto the membrane was the same or only slightly lower than beforehand on the decal substrate.

3.4 Influence of the dispersing technology and the ionomer content on the anode polarization of CCMs with two anodic catalyst layers

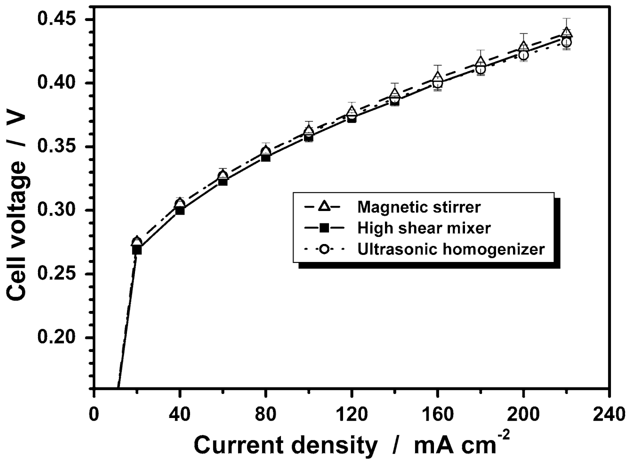

Fig. 6 Comparison of the anode polarization curves of CCMs with a Nafion content of 20% in the catalyst layer manufactured by three different ink preparation techniques. Each curve with the respective standard deviation represents the average data obtained from three individually prepared CCMs

The anode polarization of CCMs prepared from the three different catalyst inks with the same composition (i.e. 20% Nafion in catalyst layers based on 60% PtRu/C) but using different dispersing tools is shown in Fig. 6. Although these curves were not iR corrected, the different anode performances can be directly compared, as all cell resistivities (except for one single sample) were measured as being similar to one another (see below). Each curve shown in the figure represents the average of three CCMs (= measurement of six individual electrode layers; both sides of CCMs were characterized one after the other), respectively, (c.f. Sects. 2.3, 3.1). This data shows the good reproducibility of the electrode manufacturing process (small error bars), on the one hand, and on the other hand, it demonstrates that the technology used to produce the catalyst ink has no great impact on the electrochemical performance of the methanol oxidation reaction under the experimental conditions chosen for this study. This can be explained by the fact that all three dispersing technologies led to slurries containing considerable amounts of very small particles—probably being most active electrochemically—with diameters around 500 nm, although there were important differences concerning the particle size distribution and the long-term stability of the dispersions (see 3.2). As a consequence, this does not completely rule out the possibility of some non-negligible differences in terms of the water and methanol transport/barrier properties of these differently prepared catalyst layers in full-size MEAs under real DMFC operation conditions.

The electrochemical performance of CCMs with different ionomer contents has a broad flat optimum between about 20 and 40% Nafion for the catalyst used in this study

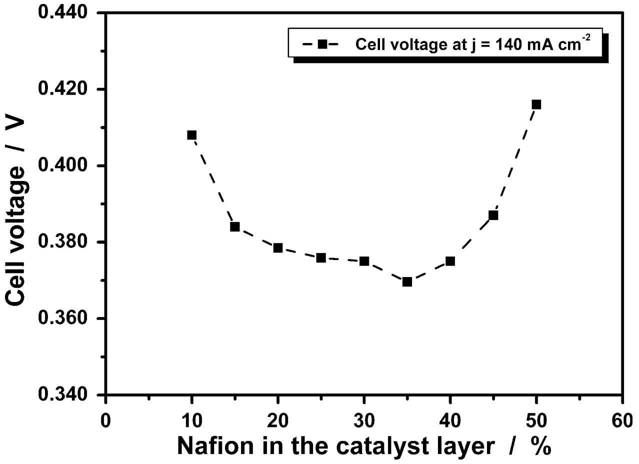

Fig. 7 Influence of the ionomer content on the anode potential at $j = 140$ mA cm^{-2} of CCMs with quasi-identical anodic catalyst layers prepared with high shear mixing; data points connected by straight lines—considerations about the uncertainty associated with this curve are provided in the main text (Sect. 3.1)

(Fig. 7). The cell voltages for all five data points in this region of composition did not differ by more than ~5 mV—and thus only by the standard deviation—from their average value (c.f. Sect. 3.1). A similar characteristic, i.e. (inverse) 'volcano' curves without a pronounced optimum, has already been observed for DMFC anodes with a different catalyst in complete MEAs [14]. The tendency that higher loaded catalysts require comparatively less ionomer [11, 13–15] indicates that there is an optimal volumetric ratio between the polymer phase and carbon [25]. Furthermore, the ohmic part of the cell resistance was observed to be independent of the Nafion content in the same composition range. For all samples up to 45% ionomer, values of 250 ± 30 mΩ cm^2 were measured, while at 50%, the cell resistance was observed to be significantly higher (>350 mΩ cm^2, not detailed here).

Although the microstructures of electrodes with the same composition produced by different routes (direct or indirect CCM, GDE and variants thereof) can result in substantial differences in the corresponding polarization curves, especially in the so-called 'mass-transport region', their influence at higher cell voltages can be rather small, as pointed out by some of the most relevant publications [3, 5–8], although contradictory literature has also been published [2, 9, 10]. Nevertheless, we expect the results of our study on the optimization of composition and ink preparation to also be relevant for the development of anodes by the GDE route, which is currently used in our institute for manufacturing electrodes for DMFC stacks of the kW class.

3.5 Performance of full-size MEAs

To verify the assumption that the development of anodes for DMFC MEAs really can benefit from the pseudo-half-cell characterization of CCMs with two quasi-identical catalyst layers, the experimental variation of the Nafion content in anodes was repeated (with slightly different steps in the ionomer concentration) on complete MEAs. For these MEAs, decal anodes were prepared as described above and joined with GDLs and invariant cathodic GDEs. The corresponding fuel cell characterization was conducted at 70 °C (instead of 80 °C used for the half-cell tests) because this temperature is close to the operating temperature of an autothermal DMFC stack of the kW class [26]. The polarization curves measured over the whole range of anode compositions from 9 to 47% Nafion did not diverge strongly. Figure 8 shows three exemplary curves, each of which represents the average characterization of three individual MEAs. Although the power density is somewhat different between the first two samples, the shape of the polarization curves is basically the same. In contrast, the $U(j)$ curve obtained from MEAs with the highest Nafion content in the anode markedly drops at high current densities. This could be correlated with the fact that these anodes with 47% Nafion have to be rather thick to achieve the same catalyst loading of ~2.0 mg cm^{-2} as the other samples, and could therefore even show some transport polarization losses in the anode [27]. This thickness effect may also account for the fact that the open circuit voltage (OCV) increased with the Nafion content of the anode (Fig. 9). Thick layers contribute to a reduction in the methanol permeation from anode to cathode, and thus the mixed potential at the cathode—which lowers the OCV—should be less important for MEAs with very thick anodes due to high Nafion content at a constant catalyst loading. The fuel cell performances at the cell voltages of 500 and

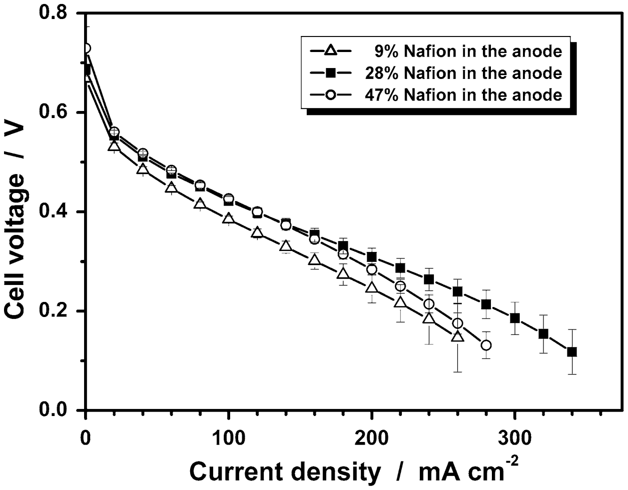

Fig. 8 Polarization curves of full-size MEAs composed of decal anodes with different Nafion contents (prepared by high shear mixing), Nafion 117 and invariant cathodic GDEs. All curves with the respective standard deviation represent the average of three independent quasi-identical MEAs ($A = 17.6$ cm^2, 1M MeOH/air, ambient pressure, $T = 70$ °C, constant flows of the reactants corresponding to $\lambda_A \sim \lambda_C \sim 4$ at $j = 500$ mA cm^{-2})

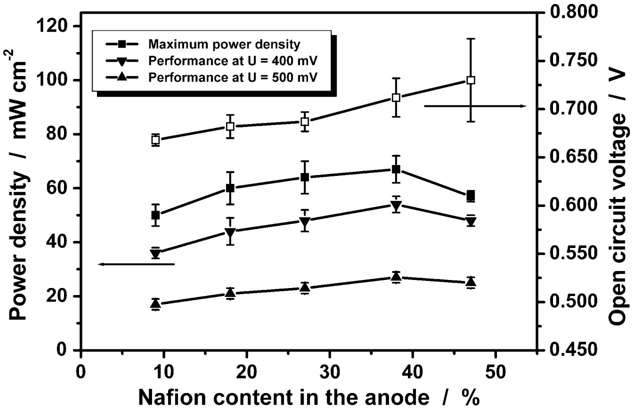

Fig. 9 Characteristic performance data of full-size MEAs with decal anodes with different Nafion contents; for further details, see the caption for Fig. 8

400 mV, as well as the peak power densities, indicate the presence of a broad plateau of beneficial ionomer content (Fig. 9). Although connecting the individual data points with straight lines suggests the presence of a distinct maximum, the differences between the values obtained with samples containing 18–37% Nafion in the anode are smaller than the experimental uncertainty.

These results basically confirm findings from the study performed using half-cell measurements on symmetrical CCMs. However, it should be noted that when three quasi-identical samples were characterized, e.g. at a current density of $j = 140$ mA cm^{-2}, the standard deviation of the cell voltage was as low as 5 mV in the case of CCM characterization, while it was more than twice as high (12 mV) for complete MEAs. Without the difference in temperature of 10 K between these two measurements (80 °C for the half-cell measurement, 70 °C for the MEA test), the advantage of CCM analysis due to its smaller experimental uncertainty would have been even more pronounced. We can, therefore, conclude that our strategy of eliminating the effects of GDLs and using two electrodes prepared simultaneously is both useful for studying the effects of the composition and manufacturing techniques on the properties of DMFC anodes. The strategy is highly sensitive and can be transferred to the optimization of complete MEAs.

4 Conclusions

Pseudo-half-cell measurements performed on symmetrical catalyst-coated membranes with two ‘anodic’ electrodes are a valuable tool for the optimization of anodes for direct methanol fuel cell MEAs, at least when these anodes have been prepared using the same decal process that has been applied for the manufacturing of CCMs. The transferability of the results obtained from such studies to anodes prepared as gas diffusion electrodes onto GDLs will have to be verified by further experiments. The main advantages of this novel technique are the increased sensitivity of the method, as both sides of CCMs with catalyst layers produced simultaneously can be studied simply by turning the cell around, as well as the fact that the effects of GDL materials on cell performance can be excluded. With three individual CCMs of quasi-identical composition, a mean standard deviation of the cell voltage as low as 5 mV was obtained during the half-cell experiment at $j = 140$ mA cm^{-2}. The experimental uncertainty derived from DMFC tests under comparable conditions was more than twice as high (Table 2).

Table 2 Experimental uncertainties associated with different electrochemical characterizations at $j = 140$ mA cm^{-2} (1 M MeOH/air, $T = 80$ °C for the CCM and 70 °C for the MEA tests, for further details see the main text)

	mV
Individual half-cell measurements performed on one single CCM configuration	0.5
Half-cell measurements performed on opposite sides of one single CCM	2–4
Half-cell measurements performed on opposite sides of three quasi-identical CCMs	5
Polarization curves of three quasi-identical full-size MEAs	12

Using this novel approach, we studied both the influences of the dispersing technique used to prepare catalyst slurries and the ionomer content on anode polarization. No distinct optimum was observed for the Nafion concentration in the anodic catalyst layer (based on 60% PtRu/C), either by the half-cell experiments performed on CCMs or from the DMFC characterization of complete MEAs. Instead, we found a very broad and flat plateau of favourable compositions between 20 and 40% Nafion. Relatively low absolute values were obtained for cell performance with the MEA components used for this study ($P_{\max} \sim 65$ mW cm^{-2}). Much better performance is expected when the same type of study is repeated with state-of-the-art materials for GDLs, catalysts, ionomer and membrane, respectively. Although the dispersing technology did not have a significant influence on anode polarization under the experimental conditions in this study, the preparation of catalyst inks by ultrasonic homogenizing was found to be advantageous compared to high shear mixing and particularly compared to preparation by a magnetic stirrer. While the choice of solvents determines the minimal particle size achievable in the catalyst ink, the dispersing technique and the associated energy input determines the extent to which this minimal size is achieved. As a consequence, ultrasonic homogenising gave rise to slurries with the narrowest particle size distribution and highest time stability, as well as to very homogeneous coatings. All of these features are necessary for the large-scale production of electrodes for direct methanol fuel cell stacks.

While the ink composition and dispersing technique represent two of the most important parameters for optimizing DMFC anodes, further research is required to elucidate the influences of other factors, such as the choice of catalyst, the equivalent weight of the ionomer, the impact of temperature and air humidity during the coating and drying process, and the hot-pressing step, in order to meet the requirements of the future mass production of high-performance DMFC MEAs.

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