In this work gas diffusion electrode (GDE) half-cells are proposed as powerful tool in fuel cell catalyst layer evaluation as it is possible to transfer the advantages of fundamental methods like thin-film rotating disk electrode (TF-RDE) such as good comparability of results, dedicated elimination of undesired parameters etc. to relevant potential ranges for fuel cell applications without mass transport limitations. With the developed setup and electrochemical protocol, first experiments on different Pt/C loadings confirm excellent reproducibility. Thereby mass-specific current densities up to 30 A mgPt\(^{-1}\) at 0.6 V vs. RHE are achieved. From a methodological perspective, good comparability to single cell measurements is obtained after theoretical corrections for temperature and concentration effects. In comparison to previous studies with GDE half-cells, polarization curves without severe mass transport limitations are recorded in a broad potential window. All these achievements indicate that the proposed method can be an efficient tool to bridge the gap between TF-RDE and single cell experiments by providing fast and dedicated insights into the effects of catalyst layers on oxygen reduction reaction performance. This method will enable straightforward and efficient optimization of catalyst layer composition and structure, especially for novel catalysts, thereby contributing to the performance enhancements of fuel cells with reduced Pt loading.

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Several approaches to close the gap between fundamental electrocatalyst evaluation via TF-RDE experiments and applied fuel cell research in single cells have already been examined. Microelectrodes for instance have been used in aqueous (to evaluate electrocatalysts intrinsic activity at high current densities) and in solid-state electrode setups (to examine the catalyst-membrane-interface). Since those solid-state electrode setups exhibit severe mass transport limitations and microelectrodes consist of bulky material, however, they do not mimic catalyst structures for real application well. Therefore, half-cell setups using gas diffusion electrodes (GDEs) have occasionally been applied from the 1990’s on to evaluate the impact of different factors on ORR performance, such as particle size, Pt-Pt content, Nafion loading, membrane ion exchange capacity and temperature. Early experiments using setups have shown the influence of mass transport issues, limiting the currents to 300 mA cm$^{-2}$ maximum. In a study about different carbon supports, Jia et al. were able to achieve current densities of about 600 mA cm$^{-2}$. Duj et al. managed to double this by adding a flow field to the back of the GDE, and Ji et al. even were able to reach 2 A cm$^{-2}$ for an alkaline system. Zalitis et al. introduced a different approach, the floating electrode setup, where a small electrode with an ultra-thin catalyst layer ($\sim$200 nm, 4.9 $\mu$g cm$^{-2}$) was placed floating on top of the electrolyte. Thereby they were able to achieve high current densities up to 185 mA cm$^{-2}$ (2000 mA cm$^{-2}$) and claimed not to be affected by mass transport limitations in the relevant range for fuel cells (0.6 – 0.8 V). However, Pinaud et al. observed transport-limitations using this technique (i) at current densities higher than 500 mA cm$^{-2}$, especially when the sample size was increased beyond 1 cm$^2$ (due to the lack of forced convective flow) and (ii) when a membrane was added to the catalyst layer to further mimic real fuel cell conditions (due to flooding). Therefore, they have developed a setup (see Figure 1A in the supporting information) introducing a flow-field that enforces a convective flow over the whole electrode area. They were able to measure ORR activities in a current density range up to 1.75 A cm$^{-2}$ (only limited by the lack of a suitable potentiostat) with good comparability to single cell experiments, proving the suitability of this method to mimic fuel cell conditions. In parallel Arentz et al. developed a setup (Figure 1B), which enables testing of low loading catalyst and catalyst coated membrane (CCM) also at higher temperatures.

## Electrochemical half-cell and instruments.—An electrochemical half-cell was specially designed to conduct measurements on GDEs in this work (Figure 1). As Pinaud et al. did not have any issues with mass transport limitations and were able to mimic fuel cell conditions also in terms of realistic catalyst layers, their half-cell (Figure 1A) was taken as a role model for half-cell design and further optimized. The cell is made from PTFE and mainly consists of an electrolyte compartment, a gas compartment and a cap. The electrolyte compartment also contains a chamber for the reference electrode. The two chambers of the electrolyte container are connected by a fine drilling, acting as a Luggin capillary (see Figure 1B). Thereby the opening is placed 1 mm apart from the electrode-electrolyte-interface ensuring a minimal uncompensated resistance ($R_u$, $R_u$ $\sim$ 0.5 Ω in 1 M HClO$_4$) between reference (RE, Ag/AgCl Metrohm) and working electrode (WE). In contrast to a conventional Luggin capillary, the drilling leaves the electric field between WE and counter electrode (CE, expanded sheet [Type G] of Ir/Ta mixed metal oxide [AN45272] on Ti, METAKEM) as undisturbed as possible. As depicted in Figure 1B, the GDE is placed between a graphite flow field (R8710, SGL CARBON, electrical resistance 13 $\mu$Ωm) and the electrolyte compartment with the active side facing the electrolyte. The graphite parallel channel flow field (see details in Figure 1A) holds similar dimensions as presented by Pinaud et al. and provides equal electric contact and gas flow over the whole electrode area from the back of the GDE. In contrast to Pinaud’s setup the contact to the carbon flow field is made with a conventional banana plug. The flow field is pressed against the electrolyte compartment by the gas compartment. Thereby a square-profile Viton sealing confines the geometrical WE area to 2 cm$^2$. Within the electrochemically active area, the GDE is not compressed as the active side is not pressed against any object, but in direct contact with the electrolyte. The electrolyte and the gas compartment can individually be purged with either Ar (99.998%, Air Liquid), H$_2$ (99.999%, Air Liquid), O$_2$ (99.998%, Air Liquid) or synthetic air (20.5% O$_2$ in N$_2$, Air Liquid), which are humidified by a commercial humidifier (Low Flow Humidification System, Fuel Cell Technologies, Inc.). The flow rate is controlled via mass flow controllers (EL-Flow Select, Bronchhorst). A cap is used to tap the electrolyte compartment and fix the CE position. The CE electrode is positioned parallel to the WE to establish an electric field as homogeneous as possible. At high current densities heating of the cell could be tracked by inserting a standard thermometer (VWR). The distance between WE and CE is decreased and fixed to 1 cm to minimize the cell resistance and thereby the resulting temperature increase. For the same reason the epoxy (UHU GmbH & Co KG) by vacuum infiltrations for approximately 10 min, and cured under ambient conditions overnight. The epoxy infiltrated electrodes were then embedded into a cylindrical puck (d = 2.5 mm) with graphite-filled thermal plastic (Technotherm 3000, Kulzer GmbH) by using a Struers mounting press (LaboPress-1, Struers GmbH). The embedding process was performed at 180°C and approximately 20 kN of pressure. The plastic embedded samples were then polished with silicon carbide papers, followed by alumina suspenisons (Struers GmbH) to reveal the cross-section of the embedded electrodes.

The revealed electrode cross-section was then imaged using a Phenom XL (Thermo Fisher) table top scanning electron microscope (SEM). The microscope was operated at 15 kV of acceleration voltage with an electron-backscatter detector for visualizing the contrast between carbon and Pt rich regions. Higher magnification SEM analyses were also performed for determining the topologies of the GDEs. Focused ion beam (FIB) milling of the GDEs was performed to reveal the cross-sectional morphologies of the catalyst layer. These investigations were performed by a Zeiss Crossbeam 540 with Gemini II optics, (Zeiss GmbH) operating at 15 kV with an in-lens detector. Before FIB milling, protective layers of Pt were deposited via electron beam (3 kV, 10 nA, for 500 nm) and subsequently via ion beam (30 kV, 300 pA, for 1 μm) on top of the desired milling sites. The milling was performed with focused Ga ions at 30 kV of acceleration voltage and a series of milling currents ranging from 30 nA to 300 pA.

### Electrode manufacturing.—The ink for the GDE fabrication comprised of a total 1 wt% solids in a solvent mixture of 20 wt% isopropanol (IPA) in H$_2$O. The solid fraction was composed of 30 wt% ionomer (Nafion D520; DuPont) and 70% Pt/C (HISPEC400; 40 wt% Pt on carbon) resulting in a gravimetric ionomer/carbon ratio of about 0.7. The ink was homogenised at 0°C with an ultrasonic horn (Hielscher) at 60 W for 20 min. GDEs were fabricated by applying the catalyst ink onto a Freudenberg H23CS gas diffusion media (230 $\mu$m thick) with an ultrasonic spraycoater (Biofluidix) on a heated stage at 85°C. The ink flow-rate and the movement-speed of the spray-head were controlled to a deposition rate of approximately 6 $\mu$g cm$^{-2}$ per deposition cycle. The Pt loading of the GDEs was measured by weighing (Sartorius Cubis, ±0.001 mg) the samples before and after the catalyst ink spray deposition.

### Catalyst layer characterization.—The cross-sectional analysis of the GDEs was performed to determine the overall thickness of the catalyst layers. The electrodes were first fixed with a two-component epoxy (UHU GmbH & Co KG) by vacuum infiltrations for approximately 10 min, and cured under ambient conditions overnight. The epoxy infiltrated electrodes were then embedded into a cylindrical puck (d = 2.5 mm) with graphite-filled thermal plastic (Technotherm 3000, Kulzer GmbH) by using a Struers mounting press (LaboPress-1, Struers GmbH). The embedding process was performed at 180°C and approximately 20 kN of pressure. The plastic embedded samples were then polished with silicon carbide papers, followed by alumina suspensions (Struers GmbH) to reveal the cross-section of the embedded electrodes.

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electrolyte volume was increased to 250 mL, so that the temperature increase in the cell could be kept below 4 K during electrochemical measurements. For all electrochemical half-cell measurements, a VSP-300 (BioLogic) potentiostat mounted with two 2A booster boards was used.

**Electrochemical measurements protocol.**—Before experiments with new catalysts or electrolyte, the half-cell is cleaned in Nochromix (Sigma Aldrich) over night, afterwards boiled in ultrapure water (Milli-Q, Merck) five times. Before each experiment the cell is boiled two times in ultrapure water again. This procedure is sufficient, as due to the higher geometric surface area and catalyst loading GDE half-cell measurements have been found to be less sensitive to contamination than RDE experiments. Nevertheless, between the experiments the cell is always stored in ultrapure water to avoid contamination. For the half-cell measurements 1 M HClO4 (70% Suprapure, Merck) is used as an electrolyte, which proved to be the optimal compromise for the half-cell measurements 1 M HClO4 (70% Suprapure, Merck) is used as an electrolyte, which proved to be the optimal compromise for GDE measurements regarding conductivity and contamination. The electrochemical protocol is based on the protocol from Pinaud et al. and is summarized in Table I. The electrochemical active surface area (ECSA) was determined by integrating the hydrogen desorption area (Hupd) of the CVs at scan rates of 50 mV s⁻¹, 100 mV s⁻¹ and 200 mV s⁻¹. The average of all three values was used to normalize for ORR activity. For ORR galvanostatic steps are conducted both forward (−0.1 mA to −4.0 A) and backwards (−4.0 A to −0.1 mA) consecutively. Firstly, the last 3 s of each step and secondly both forward and backward step are averaged to obtain the values reported on polarization curve. All experiments are conducted under ambient conditions (101 kPa, 20°C). For each loading, two samples have been tested.

**Fuel cell experiments.**—For MEA fabrication the Nafion membrane was directly deposited onto the GDEs according to the previous published work of Klingele et al. regarding direct membrane deposition (DMD). The membrane was fabricated by applying a diluted 2.5 wt% Nafion (Nafion D2021, DuPont) solution in IPA to the GDEs using an ultrasonic spraycoater (ExactaCoat, Sono-Tek). The heated stage was set to 65°C. The membrane thickness was controlled to an average of ∼13 μm per GDE (resulting in a total average membrane thickness of 26 μm for the MEA). For the anode a loading of 0.1 mgPt cm⁻² is used.

The fuel cells were assembled using 150 μm glass-fiber enforced PTFE gaskets for the anode and cathode side and a 50 μm PTFE foil as a sub-gasket between the GDEs. The sub-gasket had an opening of 2 × 2 cm, which reduced the active area of the fuel cell to 4 cm². No additional hot-pressing steps were performed. By mounting the cell with a torque of 5 Nm, the gas diffusion media was compressed by 31% for 0.1 mgPt cm⁻² and 33% for 0.4 mgPt cm⁻² cathode loading respectively. The fuel cells were operated at 80°C without backpressure on a Scribner 850e (Scribner Associates) under power-optimized conditions with H₂ (0.25 l min⁻¹) and pure O₂ (0.5 l min⁻¹) and a relative humidity (RH) of 95%. The MEAs were pre-treated with a break-in procedure consisting of repetitive potential steps at OCV, 0.3 V and 0.6 V respectively until a stable and saturated fuel cell performance was observed. The polarization data was measured galvanostatically with a step-size of 0.05 A per point and 1 min per point up to 1 A and at higher currents with a step-size of 1 A per point and 1 min per point. For iR-correction a Scribner 885-HS Fuel Cell Potentiostat (Scribner Associates) and the integrated on-line current-interrupt measurement was used to evaluate the high frequency resistance (HFR) at every recorded polarization data point.

**Results**

**Catalyst layer morphology and structure.**—The physical characteristics of the GDEs after electrochemical testing were analyzed by SEM. Representations of the cross-sectional images are shown in Figure 2 and more detailed in Figure S2 and Figure S3 in the supporting information and confirm a quite uniform thickness over the length of the catalyst layer (CL). The overall deviation of catalyst thickness over a larger field of view at lower magnification is displayed in Figure S2 in the supporting information. The thicknesses of the CLs for the GDEs are listed in Table II. The cross-sectional analysis revealed that the CL thickness does not scale linearly with respect to catalyst loading, and that the relative variations in thickness decreases slightly with CL thickness, most
Table I. Electrochemical protocol for electrocatalyst evaluation toward ORR activity. All experiments were conducted under ambient conditions (101 kPa, 20°C), with 1 M HClO₄ as electrolyte.

| Step | Electrochemical Technique | Parameters |
|------|---------------------------|------------|
| 1    | Electrochemical Cleaning  | Cyclovoltammograms (CV) | Gas purge (Flow rate) Ar (300 ml min⁻¹)  
|      |                           |            | Potential limits 0.05 – 1.2 V vs. RHE  
|      |                           |            | Scan rate 200 mV s⁻¹  
|      |                           | Number of cycles 30 - 50 (until CV is stable)  
| 2    | ECSA determination         | CV         | Gas purge (Flow rate) Ar (50 ml min⁻¹)  
|      |                           |            | Potential limits 0.05 – 1.2 V vs. RHE  
|      |                           |            | Scan rate 50/100/200 mV s⁻¹  
|      |                           | Number of cycles 3 each  
|      |                           | iR-compensation 95% in-situ correction + 5% post-correction  
| 3    | Oxide reduction            | Chronoamperometry (CA) | Gas purge (Flow rate) Ar (50 ml min⁻¹)  
|      |                           |            | Potential 0.1 V vs. RHE  
|      |                           | Time 5 min  
| 4    | ORR (O₂)                   | Open circuit potential (OCP) | Gas purge (Flow rate) O₂ (160 ml min⁻¹)  
|      |                           |            | Time 10 min  
|      |                           | Gas purge (Flow rate) O₂ (160 ml min⁻¹)  
|      |                           | Current steps (hold time)  
|      |                           | EIS frequency range f = 10 kHz – 10 Hz,  
|      |                           | EIS amplitude 10% of current (min. 10 mA)  
|      |                           | iR-compensation 100% post-correction  
| 5    | ORR (Air)                  | OCP + SGEIS | Gas purge Air (160 ml min⁻¹)  
|      |                           | Electrochemistry: see step 4  
| 6    | ECSA determination         | CV         | see step 2  
| 7    | RE potential determination | OCP        | Gas purge (Flow rate) H₂ (160 ml min⁻¹)  
|      |                           | Time ~10 min  

¹Chronopotentiometry with impedance measurement at each step.

Table II. Average thickness of spray coated cathode catalyst layers (CCL) measured from the cross-sectional images of plastic embedded gas diffusion electrodes.

| Loading mg cm⁻² | CCL average thickness (s) μm ± standard deviation (%) |
|-----------------|-------------------------------------------------------|
| 0.4             | 12.43 ± 2.64 (21.2%)                                  |
| 0.2             | 7.17 ± 1.72 (24.0%)                                   |
| 0.1             | 4.17 ± 1.01 (24.2%)                                   |
| 0.04            | 2.15 ± 0.77 (35.8%)                                   |
| 0.02            | 1.59 ± 0.56 (35.2%)                                   |

Inspection of the CL reveals a crack free exterior surface for different catalyst loadings (Figure 2). Thereby the thinner CL exhibited a web like morphology across the surface (Figure 2a). The topographic morphology observed in the Figures 2a and 2b may appear to be exaggerated due to possible topographical edge effect of the SEM. The cross-sectional image prepared by FIB also indicated that some larger pore spaces can be present within the thicker CLs. The formation of larger pores within the CL could potentially influence the mass transport by the standard deviation of measured catalyst thickness, where the deviation decreases with increasing catalyst thickness. Therefore, the CLs are slightly more uniform at higher CL thicknesses. Although the plastic infiltrated GDEs were embedded under pressure, the thicknesses of those GDEs are similar to those measured by FIB milling cross-sections. More detailed images of the representative cross-sections are shown in the supporting information (Figures S1 and S3).
transport characteristics of the GDE, which will be discussed in the further course.

**Protocol considerations.** — ECSA determination was conducted via evaluation of the $H_{\text{gal}}$ region\(^{46}\) and was determined at 50 mV s\(^{-1}\), 100 mV s\(^{-1}\) and 200 mV s\(^{-1}\) and averaged subsequently. Good comparability between the three scan rates was obtained. Therefore, it is suggested, to conduct CVs for ECSA determination at 100 mV s\(^{-1}\) for future experiments, to shorten experimental times. Previous studies revealed that a high Ar flow at the back of a GDE shifts the onset of hydrogen evolution to more positive potentials and thereby leads to ECSA experiments at low or even without flow. One alternative solution might be to flood the GDE from the back with ultrapure water, however this might affect the ongoing and continued experiments due to altered conditions at the gas-electrode interface.\(^{49}\) Hence, ECSA experiments were conducted with a minor Ar flow of 50 ml min\(^{-1}\), Figure 3 shows the Ar-CVs for different Pt-loadings and the specific Pt surface area over Pt loading.

The determined surface areas for the different loadings correspond to ECSA between 42 m\(^2\) g\(^{-1}\) and 60 m\(^2\) g\(^{-1}\) (HiSPEC4000 general specification: 60 m\(^2\) g\(^{-1}\)) and consequently utilizations between 70% and 100% in comparison to catalyst powder’s data sheet, which is in a range comparable to MEA experiments.\(^{23}\) ECSA has been compared before and after ORR and no significant difference is detected, implying no catalyst degradation during electrochemical measurements. At high current densities as acquired by the GDE method it is urgently required to determine the $R_c$ between working and reference electrode as precise as possible and correct for it to avoid errors in determining ORR activity. $R_c$ represents the total ohmic resistance between working and reference electrode and can be expressed as the sum of contributions from contact resistances between the components and ohmic resistance of the components itself (electrolyte, CL, MPL, GDL, flow field, contact).\(^{50}\) At the current of 1 A an uncompensated resistance of 10 m\(\Omega\) can lead to a deviation of 10 mV in applied potential.

\[
E_{\text{ir-compensated}} = E_{\text{uncompensated}} - IR_u
\]  \[[1]\]

In other words, considering a typical Tafel slope of 60 mV dec\(^{-1}\) this would consequently lead to an error of up to a factor of 2 in determined current density. There are several methods to determine $R_c$. In Figure 4 the influence of different methods of determining $R_c$ on the polarization curve are compared. It can be noted, that for currents higher than 200 mA (j $>$ 100 mA cm\(^{-2}\)) the accuracy of iR-compensation significantly influences the determination of ORR activity in the used system. In RDE measurements $R_c$ is usually determined at open circuit potential (OCP) just before the measurements and CVs are corrected by that.\(^{51,52}\) As the currents are reasonably small this procedure works well. Nevertheless, for GDE experiments this procedure leads to huge errors, as $R_c$ changes with increasing current density most likely due to temperature increase at the electrode surface.\(^{18}\) Therefore, Arenz et al. for instance employed CVs with positive feedback at a certain frequency to determine ORR activity.\(^{18,56}\) In our setup, this procedure also led to erroneous results and overcompensation at high currents. Additionally, it was not possible to obtain stable and reproducible CVs at high current densities. Thus, ORR was performed in galvanostatic steps with impedance measurements at each step to determine the uncompensated resistance as proposed by Pinaud et al.\(^{18}\) and typically done in fuel cell measurements. This procedure works well for currents up to 4 A, which is the limit of the deployed potentiostat with incorporated booster boards.

**Impact of Pt loading on ORR activity.** — After an optimal protocol was developed for ORR evaluation, different Pt loadings were tested. Figure 5 shows the polarization curves and Tafel plots for the conducted experiments with oxygen and air purged from the back side and 1 M HClO\(_4\) as an electrolyte. In agreement with the findings of other research groups the performance per geometric surface area improved with higher Pt-loading (Figure 5A) due to an increase in the number of active sites.\(^{51-56}\) On the other hand, the specific activity – normalized to Pt surface area – was almost similar for all tested loadings (Figure 5C), indicating two things: (a) with the proposed setup, the difference in morphology of the CL and CL layer thickness (see Figure S4 in supporting information).\(^{47-49}\) It was therefore suggested an underestimation of the ECSA, which we could also confirm (see Figure 5B) that a high Ar flow at the back of a GDE shifts the onset of hydrogen evolution to more positive potentials and thereby leads to altered conditions at the gas-electrode interface.\(^{49}\) Hence, ECSA determination on the ORR polarization profile: black – $R_c$ from impedance measurement (Nyquist-Plot), dashed lines – impact of error in $R_c$ determination ($\pm$ 5%) via impedance on ORR activity, red - $R_c$ determined at a fixed frequency (1 kHz), blue - $R_c$ taken at open circuit potential (OCP).
Figure 5. Oxygen reduction reaction (ORR) activity measured for different Pt/C loadings (HiSPEC4000) on Freudenberg H23C8 in 1 M HClO4. (A) Polarization curve purged with oxygen (results of two repetitions of each measurement are shown), (B) comparison of rotating disk electrode (RDE, Pt-poly, 0.1 M HClO4, 1600 rpm, 20 mV s$^{-1}$) and gas diffusion electrode (GDE) measurements (0.4 mgPt cm$^{-2}$, oxygen and air purged, 160 ml min$^{-1}$), (C) & (D): Tafel plots obtained with oxygen and air purged GDEs, respectively.

Discussion

Advantages and limitations of using a GDE half-cell setup for ORR performance evaluation.—In Figure 5B the advantage of GDE in comparison to RDE measurements becomes obvious. It is possible to examine catalyst activity at fuel cell working ranges (0.6–0.8 V) rather than at 0.9 V with very low current densities as in RDE. This enables dedicated evaluation especially on catalyst layer performance in a significant range of applications. Moreover, also realistic catalyst layer structures and not only dropcasted thin-films can be investigated. In comparison to MEA, it is beneficial that catalyst layer parameters such as loading and chemical and physical composition of only one electrode can be investigated independently. Thereby standard conditions can be applied and the impact of different single cell parameters such as break-in procedure, compression, membrane and temperature effects, backpressure and anode operating conditions etc. can be excluded. Moreover, with the proposed approach measurements can be executed in only a fraction of the time as done in single cell tests (∼2 h vs. 8 h for ECSA determination and polarization curves). However, the proposed setup is limited in predicting water management issues in real MEAs due to its distinct catalyst-electrolyte-interface and the low operating temperature. In MEAs it is essential to study water management as a trade-off between sufficient humidification in the CL and membrane to ensure membrane and ionomer hydration to reduce ohmic resistance and enhance proton conductivity on the one side and...
the risk of CL flooding, which leads to O2 mass transport limitations on the other side.20

The impact of CL parameters on ORR performance at high current densities.—The ORR performance is affected by (i) the intrinsic catalytic activity of the catalyst, (ii) the transport of O2 to the active catalytic centres and (iii) the accessibility of protons to the catalyst. While (i) only depends on the choice of catalyst material, (ii) and (iii) besides the operating conditions rely on catalyst layer parameters, in particular on ionomer content and distribution7–9 and the structure of the CL.53,61 In the conducted half-cell experiments, we identify no changes in the mass-specific performance with varying loading and catalyst layer thickness up to current densities of 11 A mgPt−1 (see Figure S5A in the supporting information). Above that, the low-loading catalyst exhibits a better performance, which is in agreement with previous studies in single cells and our own single cell measurements (see Figure 6), where a decrease in mass-specific performance with increasing Pt loading is observed.53,54,61 This can be attributed to a more compact CL at higher loadings, which hinders gas and water transport within the CL. This comparison between the ORR performance in GDE half-cell and MEA at high current densities confirms the absence of CL flooding and water management problems in the proposed GDE half-cell setup up to high current densities.

In terms of ionomer content and distribution Orfanidi et al.57,58 suggest that mass transport limitations can be minimized by a thin homogeneous ionomer layer around the Pt particles allowing good proton accessibility while simultaneously minimizing oxygen diffusion path length. By reducing the ionomer carbon ratio to 0.4 they achieved mass-specific current densities of about 31 A mgPt−1 at 0.76 V in MEA experiments with O2 (p = 170 kPa, T = 80°C, 100% RH).57 In a subsequent work Harzer et al.60 studied the impact of Pt particle position in carbon support and suggested that a catalyst should exhibit most Pt particles on the outer surface of the carbon black support to minimize mass transport related losses and only a small fraction inside the pores to be shielded from ionomer poisoning. In contrast, Yarlagadda et al.59 proposed that due to ionomer anion poisoning of Pt it is advantageous to segregate the ionomer from Pt particles in so-called accessible mesopores. These pores can host Pt particles and protect them from direct ionomer adsorption but still allow protons and O2 to have reasonable access to them. Therefore, pore depth and tortuosity should not be too large. They suggested that porous carbons with a preferred pore opening of 4 – 7 nm result in catalyst layers with both excellent ORR activities and transport properties and confirm this by achieving mass-specific current densities of 33 A mgPt−1 at 0.65 V in MEA experiments with air (p = 250 kPa, T = 94°C, 65% RH). As a reference, in our GDE half-cell experiment with 0.02 mgPt cm−2 we achieve mass-specific current densities of up to 30 A mgPt−1 at 0.6 V vs. RHE in O2 with not further optimized catalyst layers (Figure S5 in supporting information). Showing again that GDE half-cell experiments seem to be a suitable tool to evaluate catalysts and catalyst layer parameters at high current densities. Further work will be addressed to further improve the technique to allow more dedicated insights into the water management in the CL of MEAs.

Comparison to GDE literature.—In Figure 7 the obtained ORR activities are compared to previous works in GDE setups. Taking the performance at 0.1 mgPt cm−2 loading and comparing it to those for 0.12 mgPt cm−2 of the same catalyst with commercial GDEs reported by Pinaud et al.,18 polarization curves in the current work exhibit slightly lower intrinsic activity in the low current region, but fairly better mass transport behavior in the high current region. This reveals the suitability of GDE half-cell tests to examine catalyst layers also in different, but comparable setups if a certain protocol for evaluation is followed. Still, there is some small discrepancy to be clarified in future studies.

In comparison, Arenz et al.26,42 use a setup where a small area of catalyst (d = 3 mm) and very low loadings (currently max. 0.066 mgPt cm−2) can be tested. Figure 7A shows that severe mass transport limitations seem to affect the obtained polarization curves at potentials lower than 0.75 V vs. RHE, which could be caused by either the cell design, the measurement procedure (CVs + positive
Comparison to MEA experiments.—Due to the differences in the GDE and MEA testing conditions (temperature and reactants partial pressure), corrections have to be applied to compare experiments from GDE half-cell experiments and MEA single cell tests. Increasing the fuel cell operating pressure has three major effects on fuel cell performance: (i) on the thermodynamics, by increasing the reversible cell voltage (ii) on the electrode kinetics, by enhancing the exchange current densities due to more interactions of gas molecules with the catalyst surface per second, and (iii) on mass transfer, by improving the mass transfer limited current densities for both ORR and HOR due to higher concentration of reacting molecules on a molecular level. In general, the overall performance of PEMFC is improved with increasing the backpressure of the reactant gas. An increase of temperature on the other hand leads to a decreased reversible cell voltage (thermodynamics), a slightly enhanced kinetics for ORR and HOR as well as an improved mass transport. As the impact of temperature and partial pressure on fuel cell performance is very complex, some reasonable simplifications for thermodynamic and especially kinetic correction are made. For further understanding and more detailed insights, we refer to more dedicated literature. The derivation and calculation for the thermodynamic and kinetic correction can be found in the appendix. If both, kinetic and thermodynamic corrections are applied, a quite good accordance between MEA and GDE results is observed (see Figure 8).

In previous studies only either thermodynamic or kinetic corrections have been used, which we assume to be insufficient for realistic comparison between GDE and MEA experiments. In Figure S6 in the supporting information the impact of both corrections is displayed. Generally, it should be noted that the applied corrections have to be considered as rough estimations, as they do not cover any mass transport and other single cell effects (such as membrane resistance or hydrogen crossover).

Conclusions

GDE experiments are a powerful tool to close the gap between fundamental electrocatalysis with TF-RDE and applied fuel cell research via MEA testing. With the proposed setup it is possible to examine catalysts in relevant catalyst layer structures, current and potential ranges as in MEA tests and thereby ensure comparability, speed and precision of fundamental half-cell experiments. Moreover, the impact of the catalyst layer parameters (such as loading, chemical and physical composition) of only one electrode on fuel cell performance can be studied exclusively without the complexity introduced by the operating conditions, the membrane and the counter electrode. Therefore, GDE experiments are proposed to be a useful intermediate step between first TF-RDE experiments before upscaling to MEA testing. Nevertheless, the latter will still be essential to investigate single cell parameters such as membrane properties and water management under operating conditions, which cannot be investigated in the proposed half-cell experiments.

In the current work a protocol and cell setup are refined to enable electrochemical investigations at relevant fuel cell operation potentials. We have discussed the experimental procedure and describe essential technical considerations for reproducible measurements. The impact of Pt loading on fuel cell performance was investigated, demonstrating that specific and mass-specific activities do not change with operation conditions, the membrane and the counter electrode. Therefore, GDE experiments have to be made, the presented technique is a good starting point on the way to widespread application of GDE experiments as a bridge between TF-RDE and MEA tests for fuel cell – or other electrochemical three-phase reactions – electrocatalyst research. Future research will be focused on (a) approaching fuel cell working conditions, especially to enable insights into water management within the electrodes, (b) investigating catalyst systems who could not prove their good performance shown in RDE experiments in single cell tests and (c) coupling the technique to external analytic such as differential electrochemical mass spectrometry (DEMS) for product analysis and inductively coupled plasma mass spectrometry (ICP-MS) for catalyst dissolution.
temperature and pressure corrected potential can be calculated as follows:

\[
E(\alpha, T) = E_0(\alpha, T) + \frac{R T}{n F} \ln \left( \frac{a_{H_2} a_{O_2}}{a_{H_2O}} \right) = E^\theta(\alpha) + \Delta E^{corr}(\alpha, T) \quad [A1]
\]

With:

\[
E^\theta(\alpha) = E^\theta^0(\alpha) + \Delta \phi(\alpha) \quad \text{and} \quad \Delta \phi(\alpha) = \phi^0 \quad \text{is a function of temperature, but for the considered temperature range it can be assumed not constant. If now conditions for both, MEA (GDE) and O2 (Tafel) reactions decreases the reversible potential by approximately – 64 mV.}
\]

\[
T^\theta = 298.15 \text{ K} \rightarrow E^\theta(\alpha, T) = 1.229 \text{ V, } z = 2, \text{ } F = 96485 \text{ C mol}^{-1}
\]

\[
\Delta \phi(\alpha) = \phi^0 - 0.5 \alpha \phi^0 = -163.3 \text{ J K mol}^{-1}
\]

\[
R = 8.314 \text{ J K mol}^{-1}
\]

\[
a_{H_2O} = 1, \quad a_{H_2} = a_{O_2} = 1, \quad n = 2, \quad \phi^0 = 1.013 \text{ bar}
\]

Thereby \(E^\theta(\alpha)\) is the reversible potential at a given temperature, \(E^\theta(\alpha, T)\) the standard potential at standard conditions. The number of transferred electrons (\(n\)), the Faraday constant (\(F\)), the universal gas constant (\(R\)) and the activity of reactants (\(a\)) all contribute to the shift of the redox potential due to concentration difference (\(\Delta E^{corr}\)). Thermodynamic data is extracted from Lange’s Handbook of Chemistry.69 Actually the reaction entropy \(\Delta S\) is assumed that the concentration of species at the electrode surface remains unchanged (\(a\)), the Faraday constant and the universal gas constant are considered as not constant for a certain reaction. Also different other parameters such as the activation energy (\(\Delta G\)), the symmetry factor between forward and backward reaction (\(\alpha\)) and the temperature (\(T\)) affect the current density. Nevertheless, for our kinetic correction, those latter effects are rather negligible. \(\Delta G\) and \(\alpha\) depend on the choice of catalyst and \(T\) has an ambivalent impact on current density, as increasing the temperature leads to increased \(j_0\) but at the same time has the opposite effect on the activation overvoltage.68

Appendix

Thermodynamic and kinetic correction for temperature and O2 concentration.—

Thermodynamic correction of GDE data to MEA fuel cell operating conditions is conducted via Nernst-Equation A1. Thereby the impact of partial pressure and temperature on the redox potential (\(E\)) is considered.

\[
E(a, T) = E_0^\theta(a) - \frac{RT}{nF} \ln \left( \frac{a_{H_2} a_{O_2}}{a_{H_2O}} \right) = E^\theta(\alpha) + \Delta E^{corr}(\alpha, T) \quad [A1]
\]

Hence, the temperature and pressure difference between GDE and MEA test conditions decreases the reversible potential by approximately – 64 mV.

In contrast to thermodynamic correction kinetic correction is more complex. If it is assumed that the concentration of species at the electrode surface remains unchanged during the reaction step, the Tafel EquationA3 proved to be a good approximation for kinetics of electrolysis reactions. The impact of temperature can scarcely be seen experimentally as other positive effects of increasing the temperature (e.g. improvements in mass transport and ion conductivity) normally overlay this reaction kinetics effect.65 So the current density applied in the GDE experiments in this study have to be corrected by the factor 0.57 to correct to the MEA experiment conditions, due to the differences in reaction concentration. If both, kinetic and thermodynamic corrections are applied, then a quite good accordance between MEA and GDE results is observed (see Figure 8 and S5 in the supporting information).

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