Study of Complete Methanol Depletion in Direct Methanol Fuel Cells

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The aim of this study is to gain a deeper and more detailed insight into the corrosion processes during complete methanol depletion under direct methanol fuel cell operation. Three characteristic, consecutive phases during methanol depletion have been identified, with oxygen evolution and carbon corrosion as dominating anode reactions. Irreversible aging of membrane electrode assemblies is caused by corrosion of Ru and the carbon support of the anode catalyst layers. The latter process leads to an irreversible performance loss up to 84%, an active surface loss up to 62% and a thinning of the anode catalyst layer. For a better understanding of the aging processes, an anode impedance analysis was carried out using a transmission line model based on primary & secondary pores. The fitting analysis revealed a strong increase of the resistances associated with processes in the anode catalyst layer, including methanol oxidation kinetics, proton conductivity and mass transport. Impedance data and pore size distributions show a particularly strong degradation of (small) primary pores in the last phase of methanol depletion, suggesting a degradation process starting in the larger pores and continuing in the smaller pores.

Key development goals of direct methanol fuel cells (DMFC) are lifetime improvement and cost reduction. Despite the realization of several thousand hours of operation in a stack or a system, further research is necessary for a further increase of the lifetime, to become competitive with state of the art power source technologies like batteries.

Investigations under more stringent conditions are helpful to analyze the system limits in case of failure and get detailed information about cell degradation. Our approach is to simulate a malfunction in a DMFC stack cell by means of single cell experiments. The following difference has to be noticed: in a single cell of an operating DMFC stack, a sudden malfunction may cause a spontaneous aging process, whereas the stack current cannot be sustained any longer by methanol oxidation which requires the oxidation of alternative ‘fuels’. These candidates are mainly water, but also the carbon support of the platinum-ruthenium (PtRu) catalyst and – to a small extent – the noble metal catalyst. Because the oxygen evolution reaction (OER) takes place at anode potentials higher than 1.2 V, the anode potential increases by more than 1 V, leading to the well-known effect of cell voltage reversal. The high anode potential causes a corrosion of both carbon support and PtRu.

The reaction schemes of OER and the carbon oxidation (corrosion) reactions (COR) can be written as follows:2–5

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad U_0 = 1.230 \text{V (RHE)} \quad [1] \]

\[ C + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \quad U_0 = 0.207 \text{V (RHE)} \quad [2] \]

According to,6–8 the COR proceeds via 2 steps with the second step (eq. 2b) catalyzed by Pt or PtRu:5,6

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO}_{ad} + 2\text{H}^+ + 2\text{e}^- \quad [2a] \]

\[ \text{CO}_{ad} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad [2b] \]

Because of the slow kinetics of carbon corrosion with a very low exchange current density of about \(6 \times 10^{-19} \text{A/cm}^2\), carbon corrosion is negligible under normal operation conditions, despite the low equilibrium potential of reaction 2.

At anode potentials higher than 1.2 V, when OER starts, the following carbon corrosion reaction may also take place:3

\[ 2\text{C} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \quad U_0 = 1.230 \text{V (RHE)} \quad [3] \]

The corrosion of carbon support leads to a detachment of PtRu particles and favors the coagulation of catalyst particles. At the same time, the dissolution and re-deposition of PtRu particles, which are still in contact with the carbon phase, proceeds via Ostwald ripening.10,11 Furthermore, high anode potentials cause the corrosion (oxidation) and deposition of catalyst particles. The Pourbaix diagrams of the systems bulk Pt / water and bulk Ru / water predict Ru to be more prone to corrosion than Pt. This was confirmed by several studies,12–16 even though the mechanism of PtRu corrosion under methanol depletion is not yet fully understood. It is however certain that Ru corrodes, migrates through the membrane and deposits in the cathode.15,17

The following reaction equations were proposed by Valdez et al.:17

\[ \text{dissolution reaction (anode)}: \quad \text{Ru} + 3\text{H}_2\text{O} \rightarrow \text{Ru(OH)}_3 + 3\text{H}^+ + 3\text{e}^- \quad [4] \]

\[ \text{deposition reaction (cathode)}: \quad 2\text{Ru(OH)}_3 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{RuO}_2 + 3\text{H}_2\text{O} \quad [5] \]

The loss of Ru at the anode side leads to a decrease in specific catalytic activity of the PtRu catalyst,18,19 Moreover, the deposition of Ru at the cathode deteriorates the oxygen reduction kinetics and catalyzes the oxidation of permeated methanol. This may lead to a decrease of the cathode potential by up to 200 mV.15

The in situ analysis of anode exhaust gases via mass spectrometry allows correlating the change of electrochemical parameters with a change of gas concentrations.3,4 Wang et al. observed both \text{CO}_2 and \text{O}_2 evolution, if methanol supply was stopped under galvanostatic stack operation. They identified carbon corrosion as the main degradation mechanism. In one of our recent works,5 we applied two methods of forced methanol starvation: (i) interruption of methanol feed (like Wang et al.), (ii) substitution of methanol by water. The fundamental difference is that only in case (ii), water is present till the end of experiment, whereas in case (i), drying of cell leads to an early breakdown of cell current. This is because the presence of water is essential for all the corrosion reactions shown above. Only method (ii) leads to an almost complete destruction of the anode catalyst layer. When applying method (ii), we identified two phases of methanol...
depletion. It was shown, that the dominating reaction changes from oxygen evolution (phase I) to carbon corrosion (phase II).

In the present paper, the processes during methanol depletion are investigated by a detailed impedance analysis based on a distinction of "primary" and "secondary" pores, a concept which was introduced by Watanabe et al. According to this classification, primary pores are the smaller pores inside catalyst agglomerates and secondary pores are the larger pores outside or between the agglomerates. Tominaka et al. were the first to present an impedance analysis on DMFC catalyst layers based on primary and secondary pores. Their complex equivalent circuit allows distinguishing electrochemical parameters of primary and secondary pores in catalyst layers, in particular kinetic resistances, double layer capacitances and resistances of proton conductivity.

The results of the impedance analysis are compared to those of performance measurements, methanol stripping CVs, SEM/EDS and porosimetry measurements. The aim of this study is to gain a deeper and more detailed insight into the corrosion processes during methanol depletion.

Experimental

**MEA preparation.**— The gas diffusion layers (GDL) were produced in-house by hydrophobising commercial carbon cloth (AvCarb 1071 HCB from Ballard Materials Products) and coating it with a microporous layer containing Vulcan XC 72 carbon black (Cabot) and PTFE (TF 5032 from Dyneon) by means of an automated doctor blade technique.

For the fabrication of anode catalyst layers dispersions of carbon supported Pt-Ru(1:1)catalyst (HiSpec 13100 from Johnson Matthey, 75 wt% PtRu), Nafion solution (LQ 1115 from Ion Power) and dispersants were prepared by ultrasonic agitation. The homogenized inks were coated onto the in-house GDL by means of doctor blade technique followed by a drying step. The cathodic GDEs were manufactured following the same procedure by using dispersions of carbon supported Pt catalyst (HiSpec 13100 from Johnson Matthey, 71 wt% Pt), Nafion ionomer, PTFE (TF 5032 from Dyneon and dispersants).

The average noble metal loadings were 2.5 ± 0.2 mg/cm² on the anode side and 2.2 ± 0.2 mg/cm² on the cathode side. All GDEs were finished by over-spraying them with Nafion ionomer solution (LQ 1115 from Ion Power, ρ = 1 mg/cm²).

Finally, electrodes with a size of 42 mm × 42 mm (A = 17.64 cm²) were punched out and the MEAs were assembled by hot-pressing anode and cathode with a DuPont Nafion 115 membrane (3 minutes, 130°C, 0.5 kN/cm²).

**Electrochemical measurements.**— All experiments were performed at a temperature of 70°C and ambient pressure. For either methanol or water supply of the anode, Ismatec ‘BV-GE’ or ‘597A’ pumps were used. The flow rate of the cathode feed gas (air, nitrogen or hydrogen) was adjusted by Brooks mass flow controllers (models ‘5850E’ or ‘5850S’). The temperature was set by an in-house temperature controller.

Electrochemical experiments at electric currents < 2.4 A (j < 140 mA/cm²) were performed by means of a Zennium electrochemical workstation by ZAHNER Electric company. For higher currents, a ZAHNER power potentiostat PP241 was used.

**Polarization curves of MEAs.**— Polarization curves of MEAs were recorded in a quasi-galvanostatic mode with a scan rate of 2 mA/s. The circuit was adopted for the fitting procedure using the THALES Z.2.0 fit software of Zahner Electric company. The equivalent circuit used for the fitting procedure with the THALES software is shown in Fig. 1a.

It is based on the above-mentioned transmission line model adopted from Tominaka et al. (see Fig. 1b). As shown in one of our recent works, the consideration of primary and secondary pores is justified by (i) improved fit quality especially in the high frequency region of the impedance spectra and (ii) a good correlation of electrochemical parameters derived from the fit of impedance spectra (e.g. proton conductivity resistance in ACL) with the pore size distribution of the anode. In the following, parameters of primary and secondary pores will be indicated by the subscripts ‘pp’ and ‘sp’.

The faradaic impedances of both primary and secondary pores, $Z_{pp}$ and $Z_{sp}$, can be represented by a sub-circuit which is typical for faradaic reactions via electroosorbed intermediates and is based on a work of Harrington and Conway. The circuit was adopted for methanol oxidation by Müller et al. and is shown in the bottom part of Fig. 1b. It consists of 4 elements: (i) $R_0$, the resistance associated with the charge-transfer part without change in CO surface coverage in the ACL, (ii) $R_0$, the resistance associated with relaxation of the CO surface coverage in the ACL, (iii) $I_{ad}$, the inductance associated with relaxation of the CO surface coverage in the ACL and (iv) $CPE_d$, the constant phase element representing the pseudo double layer capacitance of the ACL.

It should be noted that the sub-circuit elements $R_0$ and $R_0$ do not represent single physical parameters, but complex terms including the potential and CO coverage dependence of net electron and CO production. Moreover, the inductive $R_0 I_{ad}$ arm of the sub-circuit which creates the characteristic inductive loop at low frequencies is not observed at high currents and not at all for the sample aged after phase III. It means that a comparison of the $R_0$ values can only be made in a limited current (anode potential) window and for a restricted number of samples.

These issues can be circumvented by the following simplification: under de conditions, i.e. $f = 0$, the sub-circuit simplifies to a simple parallel connection consisting of $R_0$ and $R_0$, because the capacitive resistance is infinitely high and the inductive resistance is zero under this condition. According to the following equation, the sum of these resistances may be defined as the kinetic resistance of methanol oxidation reaction (MOR), $R_0$, a value which can be easily interpreted as the impedance of MOR under practical operation conditions.

$$ f = 0 : \frac{1}{R_k} = \frac{1}{R_0} + \frac{1}{R_{\infty}} $$
According to this simplification and the equivalent circuit shown in Fig. 1, the following parameters were calculated separately for primary and secondary pores: (i) $R_k$, kinetic (d.c.) resistance of MOR, (ii) $R_p$, resistance of proton conductivity in the ACL and (iii) $CPE_{d}$, constant phase element representing the pseudo double layer capacitance in the ACL. The resistance of electron conductivity, $R_e$, is about 3 orders of magnitude lower than $R_p$. Therefore, $R_e$ values will not be discussed here. In addition to the above-mentioned parameters, the ohmic resistance, $R_O$, and the diffusion resistance of the anode, $R_{diff}$, were calculated.

**Methanol depletion experiments.**—The methanol depletion experiments were performed under galvanostatic conditions at 150 mA cm$^{-2}$. Each measurement started under regular conditions for at least 10 min. with an anode supply of 0.062 mL min$^{-1}$ cm$^{-2}$ 1 M methanol solution and a cathode air flow rate of 10.8 mL min$^{-1}$ cm$^{-2}$. Both flow rates are based on $\lambda = 4$ at 150 mA cm$^{-2}$. The depletion experiments were performed with three MEAs and stopped after each of three different phases of methanol depletion (see Fig. 2).

Two different ways to force methanol depletion in the single cell were applied: (i) interruption of methanol feed, (ii) substitution of 1 M methanol solution by water, maintaining the same flow rate. It should be noted, that phases II & III can only be reached if option (ii) is used, because water supply is essential to maintain carbon and noble metal corrosion reactions (see Introduction). Option (i) was therefore only used for the investigation of phase I. In one of the experiments, the anode exhaust gas concentration was measured by a mass spectrometer throughout the whole depletion experiment (see next chapter).

**Mass spectrometry.**—A quadrupole mass spectrometer (Pfeiffer Vacuum GSD 301 T) was used to analyze the anode exhaust gases during the galvanostatic methanol depletion experiment shown in Fig. 2. The anode exhaust gases, namely $O_2$ and $CO_2$, were separated from the liquid phase by means of a PTFE membrane. A continuous Helium flow was used as carrier gas. Helium was also used for calibration of gas concentrations and for maintaining a constant gas flow in the gas chamber. In order to keep the delay time between the change of cell voltage and the corresponding change of the gas concentrations as short as possible, a constant anodic flow rate has to be applied. Therefore, the exhaust gases were only analyzed during normal operation and substitution of methanol by water.

**Standard porosimetry (ASP).**—The pore size distributions of fresh and aged samples were measured by means of an Automated Porosimeter 3.1 Unit by Porotech Ltd. For this purpose, the GDLs of MEAs were removed and the cathode catalyst layers were scratched off the membrane. The remaining samples consisted of the ACL and the Nafion membrane and they contained negligible residues of micro layers and CCLs. In the next step, circular samples with a diameter of 23 mm were punched out of the samples.

Then, the porous samples were heated under vacuum for 1.5 h ($T = 170^\circ C$, $p = 2$ mbar), weighed, cooled down to room temperature, vacuum-filled with octane ($p = 2$ mbar) and weighed again. For each
of the 4 samples, 2 circular probes were stacked to attain the required minimum (octane) liquid mass of about 0.07 g. At a temperature of 40 °C, octane is removed from the samples by a step-by-step process. For each step the samples were weighed to obtain the pore size distributions (maximum of 100 steps). For the last steps at pore radii lower than 10 nm, the removing process has to be supported by applying vacuum (pmin = 2 mbar). A more detailed description of the ASP method can be found in.27

SEM/EDS analysis.— Cross sections of the MEAs were prepared by embedding the cut samples in resin. The cross sections were analyzed with a Zeiss Ultra Plus FEG scanning electron microscope. The SEM is equipped with a EDS-System from Oxford Instruments with a liquid nitrogen cooled Si(Li)-detector (30 mm²) with a resolution of 127 eV for MN Kα and an INCA Energy 350 software package.

Results and Discussion

Complete methanol depletion experiment.— This experiment was performed with a constant cell current of 150 mA cm⁻² over a period of 145 minutes. Fig. 2 shows the time-dependent anode exhaust gas concentrations of O₂ and CO₂ (green and blue lines), the gas concentration of He (carrier & calibration gas, black line) and the cell voltage (red line). Under regular conditions, it is expected that the CO₂ concentration originating from methanol oxidation is much higher than the oxygen signal (see gray area in Fig. 2). The O₂ concentration is mainly due to leaks and impurities. After 73 minutes, methanol was replaced by water (0.21 mL min⁻¹ cm⁻²; cathode feed: air (36 mL min⁻¹ cm⁻²); T = 70 °C).

Figure 2. Time-dependent anode exhaust gas concentration (He, O₂ and CO₂) and cell voltage under regular operating conditions (gray area) and 3 phases of methanol depletion (see green, blue and red areas); cell current is constant at 150 mA cm⁻²; anode feed, regular conditions: 1 M aqueous methanol solution (0.21 mL min⁻¹ cm⁻²); anode feed, complete methanol depletion: 1 M MeOH replaced by water (0.21 mL min⁻¹ cm⁻²); cathode feed: air (36 mL min⁻¹ cm⁻²); T = 70 °C.

Figure 3. Performance characteristics of a fresh MEA and MEAs aged after three phases of methanol depletion; quasi-galvanostatic U/I curves recorded at a scan rate of 2 mA s⁻¹; anode feed: 1 M aqueous methanol solution (0.21 mL min⁻¹ cm⁻²); cathode feed: dried air (36 mL min⁻¹ cm⁻²); T = 70 °C.

Phase II. Ucell = −1.5 V to −2.1 V.— A second sharp potential drop marks the beginning of phase II (see blue area) and another change of the dominating faradaic reaction. This is confirmed by the strong increase of the CO₂ signal, which indicates a severe corrosion of the carbon support in the ACL. The decrease of oxygen concentration can be explained by consumption of oxygen in the carbon corrosion process according to equation 3. The progressive damage of ACL structure, which is also proved by post-mortem analysis (see chapter 3.3), leads to a further decrease of cell voltage.

Phases II & III. As known from water electrolysis, Ru has a high catalytic activity for OER,26 but corrodes during oxygen evolution by formation of hydrated oxides.27 Thus, it is assumed that in the beginning of phase I, the OER is mainly catalyzed by Ru. With ongoing Ru corrosion, which is confirmed by post-mortem analysis (see chapter 3.3), the OER is more and more catalyzed by Pt. This process demands higher anode potentials and leads to a further decrease of cell voltage.

Electrochemical characterization before and after methanol depletion.— Single cell performance characteristics and methanol stripping CVs.— The performance characteristics of a fresh MEA and MEAs aged after three phases of methanol depletion are shown in Fig. 3. A comparison of the results for the fresh and aged samples shows an irreversible performance loss caused by methanol depletion. The decrease of percentage maximum power density is moderate after phase I (7%), but severe after phases II and II (74% and 84%), see inlet table. This result is in accordance with the pronounced CO₂ evolution during the phases II and II, indicating an irreversible loss of carbon support and structural degradation (see Fig. 2).
The same effect could be re-ported an electrochemical surface oxidation of is only 38\(\text{m}^2\text{g}^{-1}\), as shown in Fig. 5. Exemplarily, the spectra for anode potentials at high, medium and low d.c. currents which correspond to cell voltages of 100, 300 and 500 mV are shown. The fitting curves (dashed lines) based on the equivalent circuit shown in Fig. 1 match the spectra very well. Even without fitting analysis, it becomes immediately evident that both the ohmic resistance and the kinetic resistance strongly increase from phase I - III.

Fig. 6 shows the fitting results of the main parameters of the equivalent circuit presented in Fig. 1. As mentioned above, the impedance of methanol oxidation reaction is represented by the kinetic d.c. resistance, \(R_k\) (see equation 6). The parameters are plotted vs. anode potential, except the mass transport resistance, \(R_m\). In the latter case, a bar diagram was preferred because there were only 2 or 3 (or in case of phase III, none at all) measuring points per anode.

The semi-logarithmic plots in Fig. 6a/b show the kinetic resistances of methanol oxidation for primary and secondary pores. In both cases, the kinetic resistance is only slightly affected by the aging process during phase I, but increases significantly after phases II and III. In the latter case there is at least a 1 order of magnitude increase, depending on the anode potential.

The inverse slopes of the linear branches at \(U_{U_i} < 350\text{ mV}\) cannot be calculated exactly because of too less data points. However, the values of the fresh sample and the MEAs aged after phases I & II seem to be similar to the apparent Tafel slope of 115 mV reported by Gojkovic et al.\(^{34}\) (see dashed line in Fig. 6a). Only in the case of phase III, the apparent Tafel slope appears to be lower, indicating a possible change of MOR reaction mechanism. At anode potentials >400 mV, the kinetic d.c. resistance reaches a limiting value. This is consistent with the well-known limiting current of MOR, which is due to a blocking of active sites with adsorbed species like OH\(^-\).\(^{35}\)

In case of the pseudo double layer capacitance, CPE\(_a\), the situation is more complex (see Fig. 6c/d). The pseudo double layer capacitance of the secondary pores decreases with ongoing aging process (Fig. 6d), which is consistent with the decreasing active surface confirmed by methanol stripping experiments (see Fig. 4). For the primary pores, the influence of aging processes on the behavior of CPE\(_a\) may be explained by two contrary effects: The first effect is a decrease of the pseudo double layer capacitance because of active surface loss. The second effect is an increase of CPE\(_a\) caused by surface oxidation of carbon at high anode potentials. Because hydrophilic surface groups improve the wettability of the carbon surface, this may lead to an even higher pseudo double layer capacitance. The two opposing effects explain why there is a minimum of primary pore capacitance for the sample aged after phase I.

The influence of electrochemical and chemical surface oxidation on the double-layer capacitance is well-known from literature (see e.g.\(^{36,37}\)). The formation of surface groups like hydroquinone-quinone redox couples or carbonyl and hydroxide surface groups leads to an increase of surface charge and thus to a higher capacitance. Kan-gasniemi et al.\(^{37}\) reported an electrochemical surface oxidation of Vulcan at potentials >0.8 V at 65°C and a significant increase in the rate of surface oxide formation at a potential of 1.2 V. Hsieh et al.\(^{38}\) found a 79% capacitance increase by chemical surface oxidation of CNTs. Young et al. obtained an increase of double layer capacitance of graphitic carbon by a factor of 7-8, which they attributed to the generation of hydrophilic oxygenated carbon surface groups during electrochemical surface oxidation.\(^{39}\)

Fig. 6e/f show semi-logarithmic plots of the resistance of proton conductivity in the anode catalyst layer, \(R_p\). It is first of all apparent that \(R_p\) increases strongly for both primary and secondary pores. Comparison of the fresh sample and the MEA aged after phase III yields an increase by 1-2 orders of magnitude. Such an effect can only be explained by a significant degradation of ACL and/or the ACL/membrane interface. Besides the above-mentioned corrosion processes, especially carbon corrosion, a degradation of the Nafion polymer would also explain a significant increase of proton resistance. For example, the other group nearby the sulfon group is attacked by OH radicals\(^{39}\) produced during OER. Because OH radicals are
Figure 5. Nyquist plots of the anode impedance spectra of the fresh MEA (a) and the MEAs aged after three phases of methanol depletion (b-d); spectra shown by example for different anode potentials at three d.c. currents which correspond to cell voltages of 100, 300 and 500 mV; measured values marked by symbols, fit data indicated by dashed lines; $\dot{V} = 10$ mL min$^{-1}$, $f$ = 25 mHz – 20 kHz; anode feed: $V_{H2O} = 1.1$ mL min$^{-1}$, cathode feed: $V_{H2} = 50$ mL min$^{-1}$; $T = 70^\circ$C.

preferentially formed on the catalyst surface, the Nafion particles in the ACL and the ACL/membrane interface should be affected, but not the Nafion membrane. A loose contact of ACL and Nafion membrane would cause unfavorable in-plane currents of proton conduction and increase $R_p$ significantly. In this regard, $R_p$ is particularly sensitive to a loosening of contact.

Secondly, the largest effects occur after phase III for the primary pores and after phases II & III for the secondary pores. This suggests a particularly strong degradation of the primary pores after phase III, but a severe degradation of the secondary pores after both phases II and III.

Thirdly, $R_{p,sp}$ is much higher than $R_{p,pp}$, i.e. $R_{p,sp} \approx 43x R_{p,pp}$ for the fresh sample and 6x $R_{p,pp}$ for the MEA aged after phase III. The comparison of the $R_p$ values shown in Fig. 6 and those presented in our recent work$^{22}$ shows, that the $R_{p,pp}$ values are similar, but the $R_{p,sp}$ values in the present work are smaller by a factor of 40. There is however a major difference between these measurements: In case of our recent work, the impedance measurements were performed by feeding the anode with water,$^{22}$ whereas in the present work, the anode was purged by 1 M methanol solution. Methanol is known to decrease the contact angle in GDLs,$^{40}$ which particularly leads to an improved wettability of the small pores and increased conductivity of the Nafion phase within these pores. This is confirmed by a 5-fold increase of the liquid pore volume in a membrane/ACL sandwich (for preparation see chapter 2.4) if methanol solution is used instead of water. In case of 1M methanol solution, the increase is still as high as 20%.

A severe degradation of the membrane / ACL interface should also cause a strong increase of the ohmic resistance, $R_{\Omega1}$. As shown in Fig. 6g, this is evidently the case for the MEA aged after phase III. Here, $R_{\Omega1}$ reaches about 1 $\Omega$ cm$^2$, a value 4 times higher than the value of the fresh MEA. As mentioned above, both carbon corrosion and Nafion degradation can be responsible for this effect.

Fig. 6h shows a bar diagram of the mass transport resistance, $R_{diff}$. The data presented are linearly interpolated values for an anode potential of 600 mV. In case of the MEA aged after phase III, the maximum current density was too low to reach the mass transport limiting region (see also Fig. 3). For this reason, only the $R_{diff}$ values of the fresh MEA and the samples aged after phases I & II are compared in Fig. 6h. The order: $R_{diff}$ (PII) > $R_{diff}$ (fresh) > $R_{diff}$ (PI) suits well to the results obtained from the U/I curves at high current densities (see Fig. 3): because oxygen evolution can be assumed to improve the mass transport, $R_{diff}$ (PI) is about 40% lower than $R_{diff}$ (fresh). The severe carbon corrosion during phase II obviously causes an unfavorable change of the ACL pore structure, leading to a deterioration of mass transport. Thus, the mass transport resistance $R_{diff}$ (PI) is a factor of 2.4 higher than $R_{diff}$ (fresh).

Post mortem analysis of fresh and aged samples.— SEM/EDS measurements.— After the electrochemical aging procedure using complete methanol depletion, pieces were cut off the fresh sample and the aged MEAs and embedded in resin. The cross sections were investigated by SEM and EDS. SE micrographs of resin embedded
cross sections of the four MEAs (magnification: 500x) are shown in Fig. 7. Because heavy elements appear brighter, the catalyst layers (ACL & CCL) are clearly visible. The important result from these micrographs is a thinning of the anode catalyst layer after phases II and III, illustrated by the red frames. The thinning effect proves the corrosion of carbon support which is the reason for the pronounced CO₂ evolution during these phases.

The corresponding EDS pictures of ruthenium and platinum distribution are shown in Fig. 8a/b. The Ru and Pt elements are presented in red and green color, respectively. Again, the thinning effect is clearly visible (see white frames). Furthermore, a deposition of Ru in the cathode catalyst layer after methanol depletion is observed (see white arrows in Fig. 8a), which is caused by Ru corrosion in the anode and migration of Ru through the membrane. This effect has already been described in the literature. The presence of Ru in the cathode is particularly problematic, because it favors the oxidation of crossover methanol and reduces the DMFC performance.
Another important result is the deposition of Ru in the anode GDL during methanol depletion and the formation of clearly visible Ru agglomerates in some parts of the GDL (see dotted circles in Fig. 8a), which confirms the Ru dissolution and migration processes. As seen in Fig. 8b, no Pt deposition is observed in the anode GDLs. This proves that the appearance of Ru particles in the anode GDL is caused by a preferential corrosion of Ru and not an artifact due to sample preparation. The assumption of a preferential Ru corrosion but small or even negligible corrosion of Pt during methanol depletion is also supported by elemental analysis of the anode, which yielded an increase of the Pt/Ru atomic ratio during methanol depletion.

Automated standard porosimetry (ASP).—Finally, the cathode catalyst layers and the carbon cloths were removed and the residual samples consisting of the Nafion membrane and the anode catalyst layer were analyzed by automated standard porosimetry. Fig. 9 shows integral (a) and differential (b) pore size distributions in the pore size range of primary and secondary pores for the samples prepared from the fresh MEA and the MEAs aged after three phases of methanol depletion.

The decrease of specific pore volume with progressing methanol depletion (see Fig. 9a) means a densification of ACL, which can simply be explained by a collapse of the ACL pore structure caused by carbon corrosion. The shift of the secondary pore size maximum from 80 nm
The densification of ACL pore structure also explains the increase of particularly significant decrease in the specific secondary pore volume by 6% as well as categorization in primary pores (log r < 1.5) and secondary pores (log r > 1.5). Ru corrosion, this means an increase of specific pore volume by 6%. Differences after phase II results in a doubling of the ratio of primary pores after phase III, the ratio nearly achieves the previous value (1:3.8). The strong relative effect on primary pores corresponds with the significant increase of the primary pore resistances calculated after phase III corresponds with the strong relative decrease of primary pore volume obtained from ASP measurements. Both results suggest a degradation process starting in the larger pores and continuing in the smaller pores.

Quantitative results of the integral pore size distributions including a classification of pore volumes, a categorization in primary and secondary pores and the ratio of primary and secondary pore volumes are shown in Table I. Please note, that the values shown in Table I are differences of specific pore volumes in defined ranges of pore radii. The increase of specific pore volume difference of primary and secondary pores from the fresh sample to the sample aged after phase I by 6% and 14% can be partially explained by Ru corrosion, which leads to a Ru loss of 0.26 mg/cm² (33%)² and an ACL mass loss of 6%. If the microstructure of ACL and the pore volume are not affected by Ru corrosion, this means an increase of specific pore volume by 6%. Furthermore, an experimental error of ± 9% has to be considered. The particularly significant decrease in the specific secondary pore volume difference after phase II results in a doubling of the ratio of primary and secondary pore volume differences (from 1:3.7 to 1:2.0). Because of the strong relative decrease of the specific pore volume difference of primary pores after phase III, the ratio nearly achieves the previous value (1:3.8). The strong relative effect on primary pores corresponds with the significant increase of the primary pore resistances calculated from the impedance spectra obtained after phase III (see chapter 3.2).

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### List of Symbols

- $A$: geometric area of the electrodes (17.64 cm²) / cm²
- ACL: anode catalyst layer
- CCL: cathode catalyst layer
- CPE$_{ad,pp}$: constant phase element, representing the pseudo double layer capacitance in primary pores of ACL / Ω$^{-1}$ s$^6$ cm$^{-2}$
- CPE$_{ad}$: constant phase element, representing the pseudo double layer capacitance in secondary pores of ACL / Ω$^{-1}$ s$^6$ cm$^{-2}$
- CPE$_{diff}$: constant phase element, representing diffusion processes in ACL / Ω$^{-1}$ s$^6$ cm$^{-2}$
- ΔV: specific pore volume differences of ACL + membrane / cm$^3$ g$^{-1}$
- ECSA: electrochemical surface area
- $f$: frequency of sinusoidal perturbation signal / Hz
- $L_{cable}$: cable inductance / H
- $L_{cat,pp}$: inductance associated with relaxation of the CO surface coverage in primary pores of ACL / H

### Table I. Classification of pore volumes of samples prepared for ASP in the pore size range of $r = 1 – 1000$ nm (log $r = 0 – 3$); increments of log $r$ = 0.5 as well as categorization in primary pores (log $r < 1.5$) and secondary pores (log $r > 1.5$). $\Delta V / \text{cm}^3 \text{g}^{-1}$

<table>
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<tr>
<th>log ($r / \text{nm}$)</th>
<th>before aging</th>
<th>after phase I</th>
<th>after phase II</th>
<th>after phase III</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 0.5</td>
<td>0.017</td>
<td>0.020</td>
<td>0.012</td>
<td>0.016</td>
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<td>0.020</td>
<td>0.013</td>
<td>0.016</td>
<td>0.009</td>
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<td>1 - 1.5</td>
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<td>0.014</td>
<td>0.010</td>
<td>0.004</td>
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<td>1.5 - 2</td>
<td>0.055</td>
<td>0.061</td>
<td>0.023</td>
<td>0.024</td>
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<td>2 - 2.5</td>
<td>0.027</td>
<td>0.039</td>
<td>0.011</td>
<td>0.017</td>
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<tr>
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<td>0.020</td>
<td>0.013</td>
<td>0.014</td>
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<tr>
<td>0 - 1.5</td>
<td>0.030</td>
<td>0.032</td>
<td>0.023</td>
<td>0.014</td>
</tr>
<tr>
<td>%</td>
<td>100</td>
<td></td>
<td>78</td>
<td>47</td>
</tr>
<tr>
<td>%</td>
<td>100</td>
<td></td>
<td>114</td>
<td>45</td>
</tr>
<tr>
<td>ratio of primary and secondary specific pore volume differences:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 : 3.4</td>
<td>1 : 3.7</td>
<td>1 : 2.0</td>
<td>1 : 3.8</td>
<td></td>
</tr>
</tbody>
</table>

*ΔV = 0.015 cm$^3$ g$^{-1}$ subtracted (specific pore volume of Nafion membrane).
L_{ad,sp} \quad \text{inductance associated with relaxation of the CO surface coverage in secondary pores of ACL} / \text{H}

MOR \quad \text{Methanol oxidation reaction}

n \quad \text{exponent of the CPEs} / -

OER \quad \text{Oxygen evolution reaction}

P I – III \quad \text{phases I-III of methanol depletion}

Q_{MeOH} \quad \text{methanol stripping charge} / \text{mC cm}^{-2}

R_{\text{diff}} \quad \text{diffusion resistance of the anode} / \Omega \text{ cm}^2

R_{\text{e,sp}} \quad \text{resistance of electron conductivity in primary pores of ACL} / \Omega \text{ cm}^2

R_{o,sp} \quad \text{resistance of electron conductivity in secondary pores of ACL} / \Omega \text{ cm}

R_{k,pp} \quad \text{kinetic (d.c.) resistance of primary pores of ACL} / \Omega \text{ cm}^2

R_{k,sp} \quad \text{kinetic (d.c.) resistance of secondary pores of ACL} / \Omega \text{ cm}^2

R_{o} \quad \text{ohmic resistance} / \Omega \text{ cm}^2

R_{p,pp} \quad \text{resistance of proton conductivity in primary pores of ACL} / \Omega \text{ cm}^2

R_{p,sp} \quad \text{resistance of proton conductivity in secondary pores of ACL} / \Omega \text{ cm}^2

R_{r,pp} \quad \text{resistance associated with the charge-transfer part without change in intermediate surface coverage in primary pores of ACL} / \Omega \text{ cm}^2

R_{r,sp} \quad \text{resistance associated with the charge-transfer part without change in intermediate surface coverage in secondary pores of ACL} / \Omega \text{ cm}^2

R_{o,pp} \quad \text{resistance associated with relaxation of the CO surface coverage in primary pores of ACL} / \Omega \text{ cm}^2

r \quad \text{pore radius} / \text{nm}

U_{j} \quad \text{anode potential vs. DHE} / \text{mV}

U_{cell} \quad \text{cell voltage} / \text{mV}

\bar{U} \quad \text{a.c. amplitude of sinusoidal perturbation signal} / \text{mV}

V \quad \text{specific pore volume of ACL + membrane} / \text{cm}^3 \text{ g}^{-1}

Z_{sp} \quad \text{Faradaic impedance of primary pores of ACL} / \Omega \text{ cm}^2

Z_{o,sp} \quad \text{Faradaic impedance of secondary pores of ACL} / \Omega \text{ cm}^2

References