

Alteration of the distribution of the platinum catalyst in membrane-electrode assemblies during PEFC operation

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Abstract

A sufficient life time of the membrane-electrode assemblies (MEA) for polymer electrolyte fuel cells (PEFC) is necessary for using PEFC in mobile or stationary power supplies. During the life time, the electrochemical performance should be stable and the operation behavior should not change. But in real operation, the electrochemical performance decreases and the operation behavior changes. These effects are induced by a degradation of fuel cell components, which makes necessary to study the structural and chemical changes of single components affected by electrochemical stressing for understanding the degradation mechanisms and effects. The catalyst in the electrodes is the essential component dominating the fuel cell reaction. In both electrodes, platinum is used as catalyst, therefore changes of the catalyst or catalyst distribution must be investigated. The MEAs were operated in single cells in full automatic test facilities. After fuel cell operation, electrodes and MEAs were characterized physically by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and chemisorption measurements. An alteration of the platinum distribution and a migration of the platinum was observed after fuel cell operation.

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1. Introduction

Polymer electrolyte fuel cells (PEFC) are of highest interest in energy research due to the potential of direct conversion of chemical energy into electrical energy with a high efficiency [1]. Therefore, fuel cells will become an essential part of an environmentally friendly energy economy.

The central element of a fuel cell is the membrane-electrode assembly (MEA) consisting of the electrodes and a polymer electrolyte membrane. The fuel cell reaction takes place in the three phase zone in both electrodes, anode and cathode, determined by the catalyst, the membrane and the gas phase. The electrochemically active component is the catalyst.

The life time of the fuel cells is an important factor to commercialize fuel cells, where at present the status of fuel cell development cannot yet guarantee sufficient life times of several thousand of hours for mobile or transportable applications and several ten thousand of hours for stationary applications. Therefore, the investigation of degradation

mechanisms is a topic in the fuel cell research,² whereby only few publications concerning the investigation of degradation effects of polymer electrolyte membrane fuel cells exist [2–13].

Because of the central function of the catalyst its long term behavior is very interesting. Especially platinum is mainly used as catalyst in polymer electrolyte membrane fuel cells, in fuel cells with hydrogen as fuel gas platinum is applied for both electrodes, in direct methanol fuel cells (DMFC) platinum only for the cathode. In general, the stability of carbon supported catalyst is an important technical problem, whereby impurities are of great influence [14]. The mobility of platinum under reaction conditions is well known. Studies on noble metal surfaces show a decrease of the surface roughness [15–19] under reaction conditions, a fluctuation of steps on well defined single crystal surfaces [20] or the direct movement of platinum atoms on the surface [21,22]. This shows clearly the mobility of platinum on platinum. Also a mobility of platinum on highly oriented pyrolytic graphite (HOPG) [23] was observed. Studies of fuel cell electrodes with carbon supported platinum cata-

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lysts [4,24,25] show the platinum mobility under fuel cell conditions. The mobility of the platinum is an important influence in the preparation of highly dispersive platinum catalysts [26], but this mobility can effect a degradation of the catalyst under fuel cell operating conditions [27–29]. To investigate the degradation of the catalyst, fuel cell experiments must be supported by physical analysis. For this purpose, a lot of characterization methods are helpful.

2. Experimental

2.1. Sample preparation

For the experiments, commercial electrodes and electrodes prepared with the DLR dry spraying technique were used. In contrast to the preparation technique of the electrodes from a suspension containing catalyst, the DLR manufacturing technique is a dry process avoiding solutions and complicated process steps. The DLR dry spraying technique [2,30–34] is a consequent further development of the manufacturing technique for alkaline fuel cell electrodes [35–42], with a new deposition type of the powder mixture for the reaction layer. In both electrodes, commercial electrodes and the DLR electrodes, a carbon supported platinum catalyst is used. To prepare the membrane-electrode assemblies for the fuel cell operation the electrodes were hot-pressed with a Nafion[®] membrane from Du Pont.

In the investigated MEA Nafion[®]1135 membranes are used, coated with a mixture of 80 wt.% carbon supported platinum catalyst (20 wt.%) from E-Tek and 20 wt.% PTFE. As gas diffusion layers (GDL) on both electrodes, anodes and cathodes, single sided E-Tek backings are used. In addition, some experiments were performed with commercial electrodes (E-Tek electrodes with 20 wt.% Pt in the carbon supported platinum catalyst).

2.2. Electrochemical tests

The MEAs were electrochemically tested in single cell configuration. The active area of the MEAs was $4.8\text{ cm} \times 4.8\text{ cm}$. The tests were performed in automated fuel cell test facilities [2,43]. The test facilities allow the choice of operation conditions in a wide range of parameters. Some of the electrochemical tests have been performed in segmented cells, which allow the measurement of local current densities. In this segmented cells the active are of $4.8\text{ cm} \times 4.8\text{ cm}$ are divided into 4×4 quadratic segments, whereby the current values are recorded for each segment separately. At DLR, the same segmented cells are used for the investigation of hydrogen supplied polymer electrolyte membrane fuel cells as well as for the investigation of direct methanol fuel cells. More details of these segmented cells are described in [43]. The membrane-electrode assemblies are electrochemically characterized in the test facilities by $V-i$ curves, measurement of the local current densities and electrochemical impedance

spectroscopy. For all measurements with the MEAs prepared by the DLR dry spraying technique, the segmented cells were used for the electrochemical tests. The commercial electrodes were tested in the non-segmented cells.

2.3. Physical characterization

After preparation and after electrochemical stressing by fuel cell operation, the MEAs were investigated by scanning electron microscopy (SEM) [44] combined with energy dispersive X-ray spectroscopy (EDX) [44], X-ray photoelectron spectroscopy (XPS) [44] and porosimetry (with mercury penetration) [45,46]. For the SEM and EDX measurements, a Zeiss Gemini microscope (LEO) was used in combination with a NORAN VOYAGER 3000 EDX-detector. The SEM used allows high magnification imaging at low and high beam voltages (1–30 keV). The XPS measurements were performed in a XSAM 800 (Kratos)—the XPS equipment is described in more details in [47]. XPS yields information about the chemical composition of the surface and the method shows a very high surface sensitivity. In contrast, EDX has a low surface sensitivity and yields information about the bulk composition of the range close to the surface. SEM yields information about the surface structure and gives information about the bulk character.

3. Result and discussion

3.1. XPS-measurements on commercial electrodes

The high surface sensitivity of the X-ray photoelectron spectroscopy requires a well defined surface for the analysis. The electrodes in a hot-pressed and operated MEA stick on to the membranes. Therefore, with such MEAs, the separation of the electrodes from the membrane are not well reproducible and the surfaces of the separated electrodes are not well defined. Especially for the DLR MEA for PEFC applications, this is because the reaction layer is coated directly onto the membrane and the membrane with the reaction layers are pressed together with the backings [2], whereby the reaction layers stick better on the membrane than on the backing structure. Consequently, the DLR MEAs cannot be separated in a way that the interface between reaction layer and membrane can be analyzed by XPS.

In contrast to the DLR electrodes, in the commercial electrodes the reaction layer and the gas diffusion layer are a unit. For the XPS measurement, commercial electrodes were cold-pressed with a Nafion[®] 117 membrane and operated for few days under normal fuel cell conditions. The fuel cell was operated at $80\text{ }^\circ\text{C}$ with the hydrogen feed stream humidified by passage through a wash-bottle at a temperature of $80\text{ }^\circ\text{C}$. The oxygen was not humidified. Pure hydrogen and oxygen was used, both at 2.0 bar. Concerning the hydrogen “dead-end” operation was used whereas the oxygen was adapted to the requirement of different current

densities. The oxygen flow at the gas outlet of the fuel cell was kept constant. The overstoichiometry of the oxygen decreases with higher current densities and was approximately 1.4. After operation, the electrodes were separated from the membrane and analyzed by XPS, whereby the electrochemical experiment was finished with an operable MEA (active electrodes). The MEA was operated for few days at a constant potential of 500 mV.

By alternately recording XP spectra and ion etching the surface (Ar^+ -ions, 2.5 keV) depth profiles of the chemical composition were measured. The ion etching time between the measurement of two XP spectra was increased every five cycles by the factor three in order to record the chemical composition up to a depth of few 10 nm. The measurements were performed on commercial electrodes which have a polymer covered surface [2,33]. As a consequence of the polymer covering film the Pt signal increases in the depth profile measurement caused by the partial removal of the polymer film by ion etching and X-ray-induced decomposition of the polymer.

The depth profile measurements of an unused electrode and the electrodes from the not-hot-pressed, used MEA is shown in Fig. 1. The decrease of the fluorine concentration in the depth profiles is induced by the removing of the polymer covering film and by the radiation-induced decomposition of the PTFE. Consequently, the carbon concentration increases in the depth profile measurements, especially caused by a lower efficiency of the ion etching for carbon compared with the other elements in the electrodes. The depth profiles of the new electrode and the used cathode are very similar. The concentration of the fluorine and platinum in the used cathode is slightly decreased compared with the new electrode. In contrast, the depth profile of the anode is significantly different from that of the new electrode. At the beginning of depth profiling on the hydrogen electrode, a lower oxygen concentration than on the new and on the oxygen electrode is measured. Also the fluorine concentration in the anode is lower than in the new electrode; the carbon concentration in the anode is higher. The higher carbon concentration can be explained by residuals of organic impurities or PTFE decomposition. On the cathode side, similar organic impurities would be oxidized and removed in form of carbon monoxide or dioxide. The carbon detail spectra shows that on the anode, the carbon signal in the region of the C1s signal of graphite or carbon black is significantly increased [2]. In the anode, the concentration of carbon in PTFE is approximately 25–30% lower than in new electrode. In the depth profile of the anode, a higher initial carbon concentration is observed. In addition, the PTFE is partially covered by the other carbon compound and will be recovered in the depth profile. Therefore, the change of the fluorine and carbon concentration in the depth profile of the anode is not so significant as observed in the depth profiles of the other electrodes. For this investigation, the main important difference in the depth profiles is that in the electrode, which was used as hydrogen electrode,

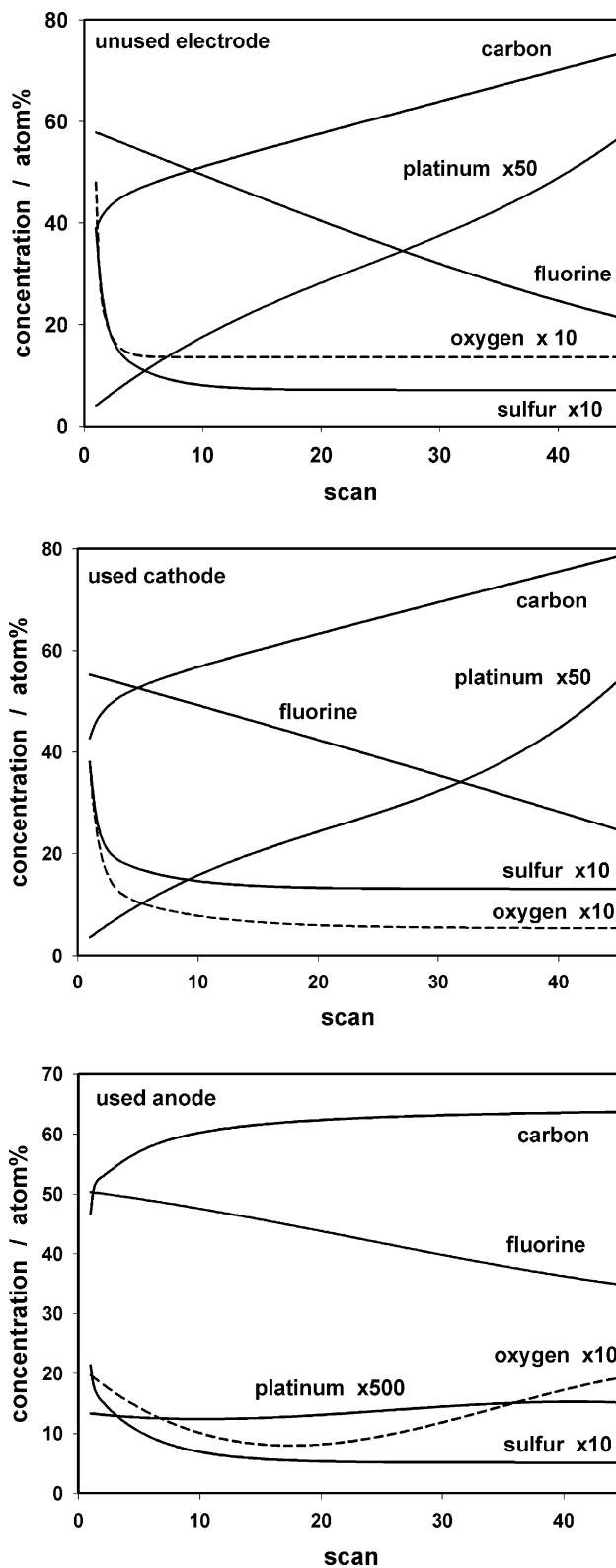


Fig. 1. Depth profile measurement of a commercial electrode, as delivered (at top), after operating as cathode (in the middle) and after operation as anode (at bottom).

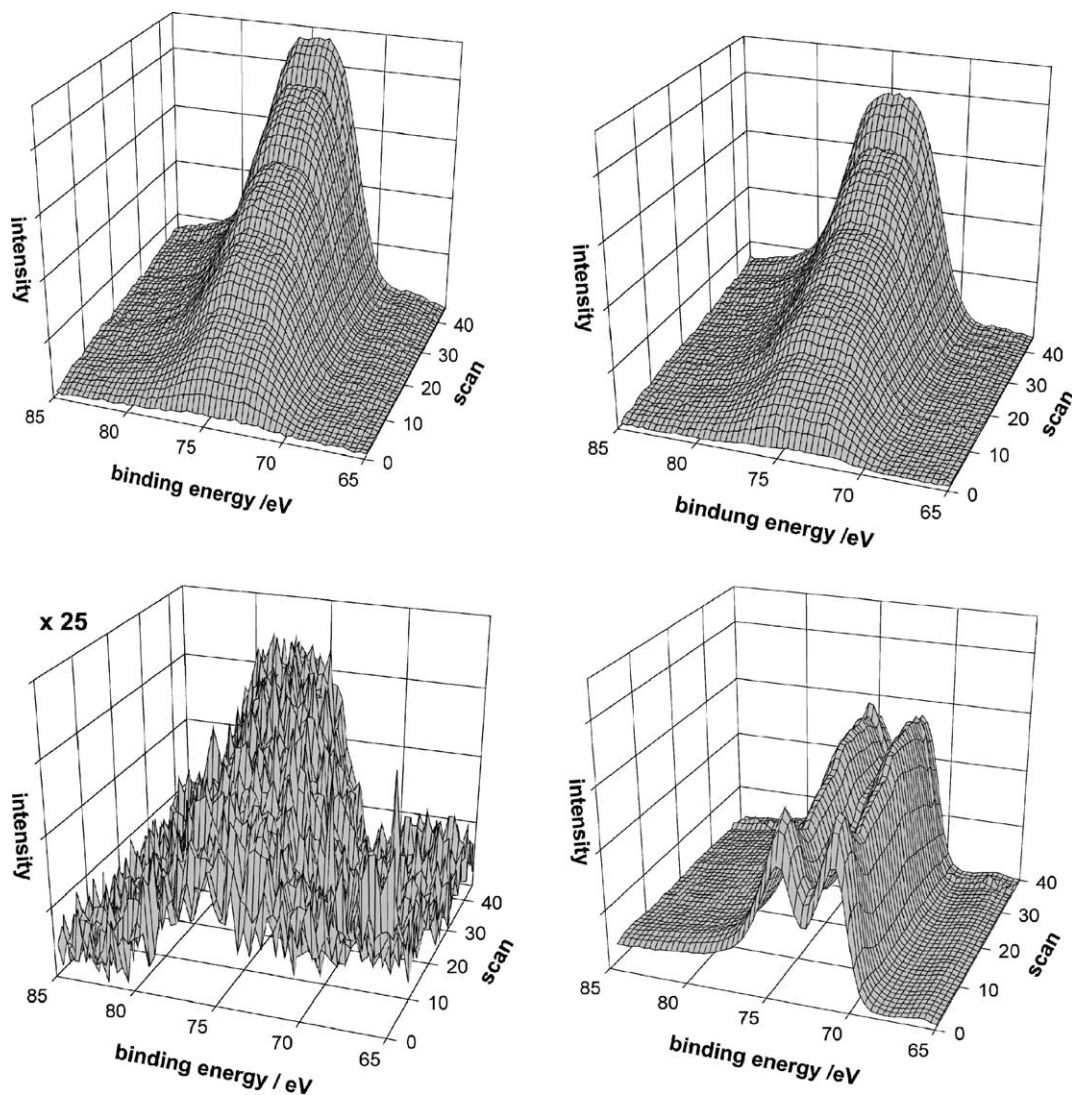


Fig. 2. Pt 4f XP spectra recorded during depth profile measurement of a commercial electrode as delivered (at top, left side), after operating as cathode (at top, right side), after operation as anode (at bottom, left side) and after electrochemical stressing in aqueous electrolyte (at bottom, right side).

the platinum concentration on the surface is dramatically changed.

The Pt 4f spectra of four electrodes recorded during depth profile measurements are presented in Fig. 2. The spectra at the top on the left side are recorded during depth profile measurement of a fresh electrode, the spectra at the top on the right side are recorded for the cathode, used in the experiment described above and the spectra at the bottom on the left side are measured for the anode used in the same experiment. The spectra shown at the bottom on the right side are measured after electrochemical stressing in a test cell with aqueous electrolyte. The corresponding electrochemical experiment will be described later.

The platinum concentration on the anode is reduced significantly. The Pt 4f spectra of the anodes were enlarged by a scaling factor of 25 as compared to the spectra of the cathode. At the beginning of depth profiling, the platinum

concentration in the hydrogen electrode is close to the detection limits of the XP instruments and increases during the depth profiling by a factor of 2–5. The decrease of the total platinum concentration in the anode can be explained by a change in the platinum distribution.

If the separate platinum clusters associate building up larger three-dimensional clusters, also less platinum stays on the surface providing XPS signal. Another potential explanation is that the platinum moved to the interface between the membrane and the electrode, adhering to the membrane at separation of the electrode from the MEA. The membrane was not investigated by XPS, so it cannot be decided which platinum diffusion mechanism is responsible for the reduced platinum content of the investigated electrode surface.

An alternative explanation for the observed reduced platinum concentration can be given by a covering of the electrode. In fact, on the anode an increased concentration of

carbon in a CH_x binding configuration is observed which may be induced by the electrochemical decomposition of PTFE [2,41,42] or by organic impurities in the fuel gas, but, if the reduction of the detectable platinum concentration is induced by covering with the organic impurities, the platinum signal must significantly increase with the depth profile measurement. In addition, the electrochemical activity should be reduced when the catalyst is covered and poisoned to such a dramatical degree. In the experiment, the electrochemical performance is not significantly reduced during the operation time. If the platinum has moved to the membrane surface, the electrochemical performance of the anode will not decrease, but this can improve the performance caused by the better contact between catalyst and electrolyte. Therefore, taking all potential facts into account, we conclude that the drastically reduced platinum concentration in the surface region of the anode is not effected by the covering of the electrode surface with organic impurities.

In another experiment one of the commercial electrodes was electrochemically stressed by performing cyclic voltammometry (100 mV/s, 0–1.5 V versus RHE). During the recording of the cyclic voltammograms, the peak current value of the platinum oxidation and platinum oxide reduction signal increases nearly linearly during the operation time. For details of this experiment see [11]. The electrode was investigated by XPS following this electrochemical experiment. The Pt 4f spectra recorded for this

electrode are shown at the right side at the bottom of Fig. 2. The platinum concentration is significantly increased on the electrode surface compared with the new electrode. In addition, no significant change of the platinum concentration during the depth profile measurement can be observed. An alteration of the platinum distribution during cyclic voltammetry measurements was also found with nuclear magnetic resonance (NMR) [48].

The formation of a homogeneous platinum distribution can be explained by the removal of the PTFE film as well as by alteration of the platinum distribution. During the activation of alkaline fuel cell anodes with a nickel catalyst, the change of the PTFE is one of the determining factors [41,49]. Caused by the change of the PTFE distribution the catalyst surface becomes open for the reaction, but in the XP spectra no significant increase of the catalyst concentration can be observed [41]. During the activation the PTFE film becomes leaky, which allows the electrolyte to contact the catalyst. Therefore, the formation of the homogeneous platinum distribution as result of the alteration of the PTFE distribution is not plausible. Consequently, the homogeneous platinum distribution must be explained by the alteration of the platinum distribution during the electrochemical experiment.

3.2. Investigations on DLR-electrodes

Considering the problem of separating reproducibly the electrodes from membrane-electrode assemblies prepared

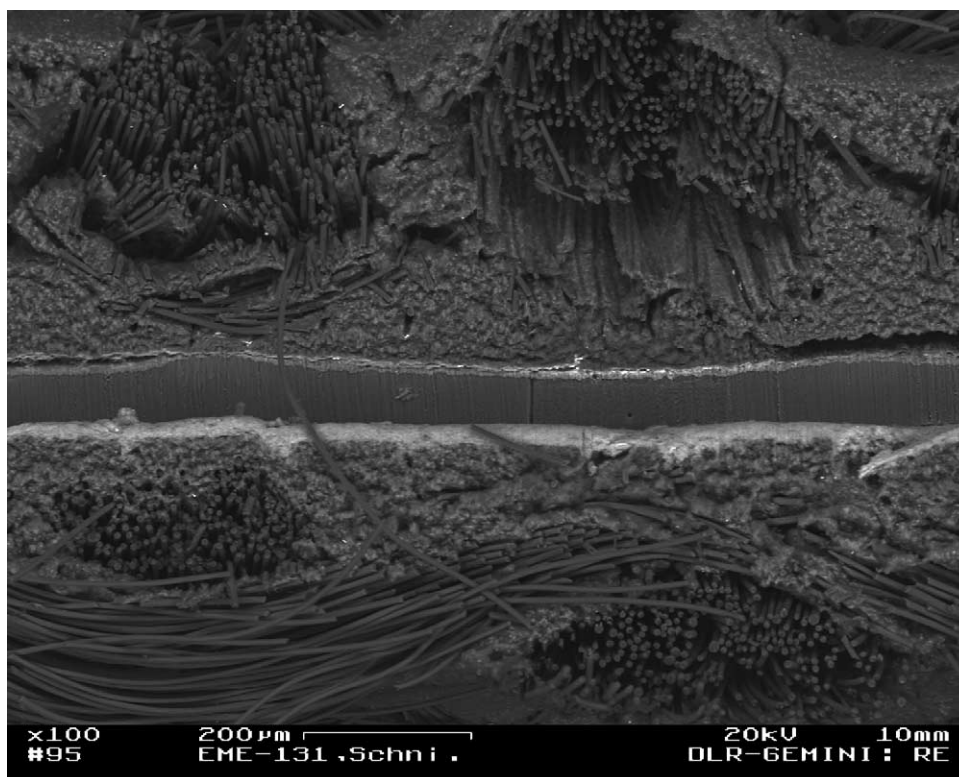


Fig. 3. SEM image of a cross-section of a used MEA prepared by the DLR dry spraying technique.

with the DLR spraying technique, the electrodes in DLR MEAs were investigated by scanning electron microscopy. These investigations were performed on cross-sections of stressed and unstressed MEAs. In contrast to the XPS measurements, the surface sensitivity of the EDX analysis is significantly lower, but the SEM/EDX gives additional infor-

mation about the structure. Therefore, the information about the platinum distribution determined by XPS and SEM/EDX measurements can differ.

The MEAs prepared by the DLR dry spraying technique were stressed in single cells under normal fuel cell operation conditions as well as under special conditions.

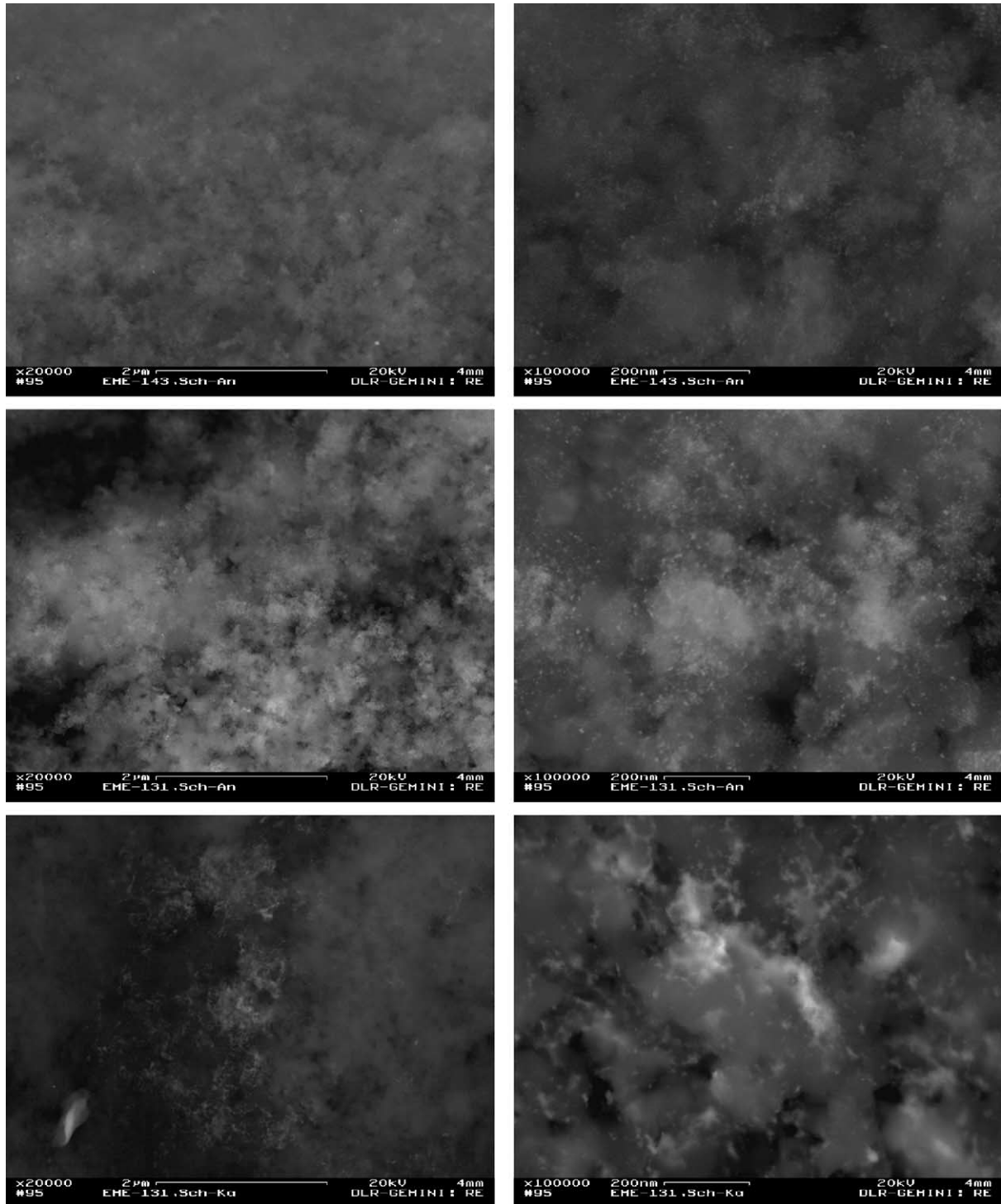


Fig. 4. Reaction layers in a MEA prepared by the DLR dry spraying technique imaged by SEM: left side magnification 20,000, right side magnification 100,000; at top, reaction layer of a fresh MEA; in the middle, the anodic reaction layer and at bottom the cathodic reaction layer of an electrochemically stressed MEA.

A MEA with two equal electrodes which have a Pt-loading of 0.25 mg/cm^2 on a single sided backing was hot-pressed with a Nafion® 1135 membrane. The fuel cell tests were performed in a stainless steel cell with an active surface of 23 cm^2 . The test cell is segmented into 16 areas on the anode side, whereas the cathode is not segmented. With this set-up, the current density in the cell can be measured on-line in fuel-cell operation. The MEA was electrochemically stressed at 80°C with pure hydrogen and oxygen. The gases were not humidified. The anode side was purged by opening the outlet valve with pulses of 0.5 s every 900 s and similarly the outlet valve on the cathode side was opened every 120 s for 0.5 s. For the start-up, the MEA was humidified directly with liquid water injection within the test cell and afterwards stressed electrochemically at 500 mV cell voltage. After operation for few days, the SEM images showed no significant alteration of the platinum distribution, but a slight change in the cathode cannot be excluded.

In a second experiment, the operation mode was changed after 80 h. The anode was operated in dead-end mode and the cycle time between the purging of the cathode gas volume was increased to 240 s. With these operation conditions, the anode side was flooded by reaction water and the cell current decreased. The current density measurement has clearly shown that the cell passivation starts from the lower part and extends to the top with increasing level of liquid water on the anode side. So, the decreasing current of the cell can be related to a decreasing active area of the anode. After 30 h under these operation conditions, the anode outlet valve was opened and water was blown out from the anode

side. The current distribution measured with the segmented cell shows that the cell is flooded starting from the bottom. During the operation time, the water level increases until the cell is completely flooded. The current density maximum shifts from the middle of the active area at the beginning of the experiment to the region at the highest point in the cell. After this experiment, the MEA has not achieved the former electrochemical performance.

Fig. 3 shows a cross-section of a used MEA. The different layers in the MEA, gas diffusion layer at the top and at the bottom, the reaction layers of the anode and of the cathode, imaged bright, and the polymer electrolyte membrane in the middle, can be clearly distinguished. The Fig. 4 shows reaction zones imaged by SEM with a higher magnifications of such cross-sections. On the left side, the reaction zone was imaged with a magnification of $20,000\times$ on the right side the same region was imaged with magnification of $100,000\times$. At the beam energy used (20 keV) in the SEM images, the polymer structures become transparent and the image is more determined by the distribution of the heavy elements like platinum.

At the top, the reaction layer of a fresh MEA is displayed, in the middle the anodic reaction layer of the stressed MEA and at the bottom the corresponding cathodic reaction layer. The SEM images of the unstressed and the stressed anodic reaction layers are very similar and show a highly dispersed platinum distribution, which is imaged as a bright cloud. The cloud structure for the platinum distribution is also observed in the cathodic reaction layer of the stressed MEA, but it is beginning to vanish. In contrast to the anodic reaction layer,

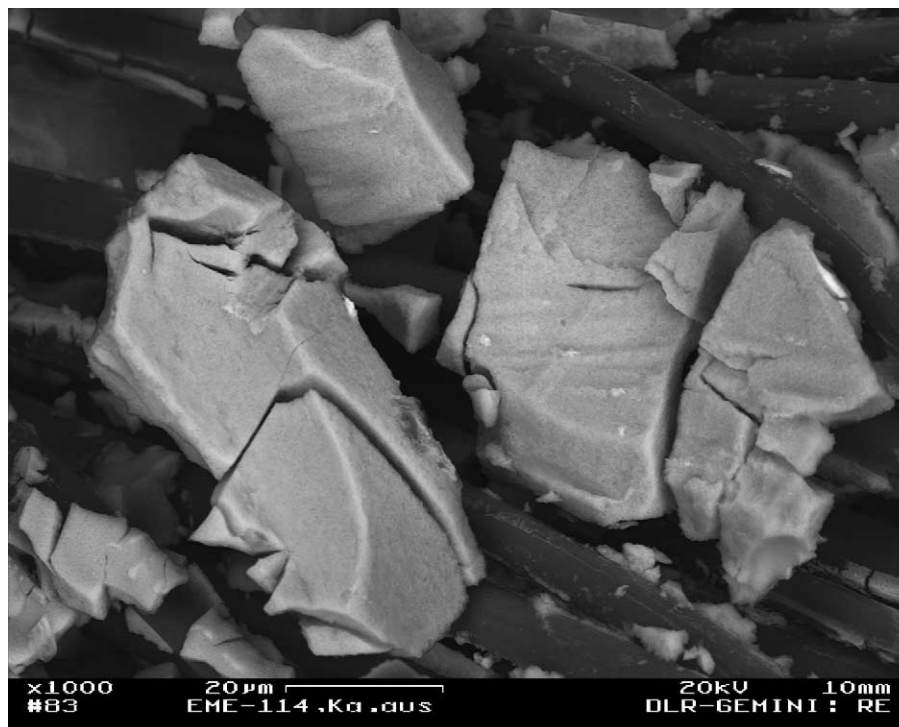


Fig. 5. Platinum oxide particles on the backside of the cathode gas diffusion layer, imaged by SEM.

in the cathodic reaction layer an accumulation of the highly dispersed platinum can be observed yielding sharp bright points, which indicates growth of some of the platinum particles in the cathodic reaction layer. The more significant formation of bigger platinum clusters in the cathode than in anode was also observed in the X-ray diffraction study [24].

This indicates that the platinum changes with the operation under the described conditions. It can be suggested, that these unfavorable operation conditions are irrelevant for the real fuel cell operation, which is correct if only the overall conditions are considered, but not for the local conditions in a MEA especially in a stack. In a further experiment, the operation conditions were set that one part of the gas volume was flooded by water and controlled by the current density measurements in the segmented cell. Under these conditions, the accumulation of platinum was observed only in the cathodic reaction layer opposite to the flooded anodic gas volume, in the other parts of the cathodic reaction layer this significant alteration of the platinum distribution could not be observed.

On the backside of the gas diffusion layers of the cathodes deposited particles were observed after this experiments. Therefore, additionally to the SEM investigations of the cross-sections, the backsides of the GDL directed to the bipolar or end plates were investigated. The particles on the backside of the cathode GDL were identified by EDX as platinum oxide. Fig. 5 shows such a platinum oxide particle with a size of approximately 50 μm . The platinum oxide particles are formed during the fuel cell experiments. The distribution of the big platinum oxide particles is strongly inhomogeneous, particularly on the area of the cathode backing which was opposite to the water flooded anode area where the big particles were formed. In the area opposite to the “dry” anode part, no big platinum oxide particles were found. On the anode backing no platinum or platinum oxide could be observed.

4. Conclusions

In the XPS measurements on the non-hot-pressed MEA with commercial electrodes a significant change of the platinum concentration is observed in the anode, in contrast the concentration in the cathode is nearly the same as in an electrochemical unstressed electrode.

The SEM/EDX investigations of the MEAs prepared with the DLR dry spraying technique showed that the platinum distribution is altered on the cathode but not on the anode.

This SEM/EDX result measured for the DLR MEA and the XPS measurements on the non-hot-pressed MEA with commercial electrodes seems to be in conflict. But the information derived from both methods are different, as are the electrochemical experiments.

In the experiment with the commercial electrodes in a MEA, which was not-hot-pressed, the electrical contact between the electrodes and the membrane are weaker than in

the experiments with the MEAs prepared by the DLR technique. Consequently, the potential drop on the interface between electrodes and polymer electrolyte membrane in the non-hot-pressed MEA is higher than with the DLR-MEAs.

With the XPS measurements, a very thin layer of a few nm can be investigated, whereby the measurement yields no lateral resolution, but a high resolution in depth extension. The SEM measurements of the cross-section do not allow to investigate the platinum distribution with a comparable resolution on the interface between membrane and reaction layer, but yield with high lateral resolution information about the platinum distribution in the reaction layer. From the formation of large platinum oxide particles on the backside of the gas diffusion layer only of the cathode, it can be concluded that the movement of the platinum is correlated with the electric field gradients. The platinum movement is directed from the anode to the cathode side as expected for the movement of platinum ions. A second effect parallel to this movement in the electrical field is that the stability of the platinum particles increases with the particle size, therefore, the accumulation of platinum particles by random movement of platinum atoms results in a more stable platinum distribution as observed by SEM in the reaction layer. In fuel cell operation, the impedance of the MEA is mainly determined by the impedance of the cathode. The impedance of the anode is significantly lower [50]. Therefore, in a typical MEA the electric field gradient in the anode is very low. The field gradient in the cathode is higher and consequently so is the mobility of the platinum in the cathode compared to the anode as observed with the SEM. The correlation of the alteration of the platinum distribution induced by electrochemical stressing and the electrical field gradients is adverse, because the platinum distribution on the critical electrodes with higher potential drops are more changed than the platinum distribution in electrodes with low potential drops. As consequence, the alteration of the platinum distribution can become a self-energizing effect.

Considering the influence of the electrical fields and the information, which can be derived from XPS measurements the results with the non-hot-pressed MEA fit the SEM results of the DLR-MEA. Caused by the weak electrical contact between anode and membrane the potential drop to the membrane yields higher electric field gradients than in a typical MEA. Consequently, the mobility of the platinum in the investigated zone becomes high and the platinum will be depleted on the anode surface, where the platinum is moved in the direction of the cathode. Therefore, a deposition of platinum from the anode surface onto the membrane surface is probable. In contrast to the anode, the weak electrical contact between electrode and membrane does not yield to a movement of the platinum from the cathode to the membrane, but the electrical field will support the movement of platinum into the cathode interior. But compared to the potential drop on the interface, the electrical field in the cathode is low, therefore, the platinum distribution does not alter significantly on the cathode surface in the experiments.

The XPS investigation of the electrode stressed in aqueous electrolyte, as well the SEM investigations with the flooded gas volumes demonstrate clearly that the platinum movement is supported by the physical presence of liquid water. In technical fuel cells especially in fuel cell stacks with a broad range of local operation conditions domains of the electrodes are flooded by water, whereby these regions can be heterogeneously distributed. Therefore, the alteration of the platinum distribution is a real problem in PEFC, but cannot be quantified at the current state of knowledge. Caused by the influence of the liquid water phase the operation conditions must be controlled and restricted to avoid disadvantageous operation conditions, which must be considered by the design of fuel cell stacks.

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