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Atomic force microscopy and infrared analysis of aging processes of polymer electrolyte membrane fuel cell components

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ABSTRACT

In this contribution, the possibilities and limits of atomic force microscopy (AFM) for investigation of fuel cell component degradation are evaluated. In particular the adhesion force and dissipation energy of the surface measured by a material sensitive AFM technique – the HarmoniX-mode (Bruker Corp.) – have been used as a measure for the relative polytetrafluoroethylene (PTFE) content of surfaces and could be quantified by calibrating with sample of known composition. Differently operated samples with microporous layers (MPLs) of commercial gas diffusion layers (GDLs) were investigated before and after operation and were compared to artificially aged and reference samples. A larger degradation of the cathode material compared to the anode was always found. As an additional example for the potential of AFM and infrared absorption spectroscopy (FTIR-ATR) the local PTFE content of a cell with a segmented anode flow field has been investigated. The results of PTFE loss at MPL and electrode surfaces from AFM measurements and infrared spectroscopy delivered different results which were explained by the distinct information depth of both methods. The large relative differences of PTFE content of the different segments were correlated with the mechanical properties of the special design of the segmented cell.

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1. Introduction

In polymer electrolyte membrane fuel cells (PEMFCs), gas diffusion layers (GDLs) are responsible for gas distribution, electronic contacts and mechanical protection of electrodes. GDLs should have a good electronic conductivity, an open pore structure for supplying catalytic layers with gases, enabling gaseous water transport, as well as expelling excess liquid water. Therefore, typically a mixture of powder containing mainly carbon particles and polytetrafluoroethylene (PTFE) is used for providing hydrophobic surfaces and good electronic conductivity. The addition of the microporous layer (MPL) of about 50 µm thickness with a dense nanometer sized structure and with a range of pore diameters of 0.02–0.5 µm [1] has proven to improve efficiency as well as operational stability of the fuel cell, although a comprehensive explanation of its function is still missing. The GDL substrate, in comparison, possesses a macro pore size of 1 µm with a typical thickness of 100 µm [2,3]. The role of the MPL may include the following functions for the cell [4–7]:

- (1) Flooding is reduced due to a smaller pore size and an enhanced hydrophobicity which leads to a higher saturated vapor pressure inside the MPL than inside the GDL.
- (2) The hydrophobicity of the MPL repels water to the membrane side effectively hydrating the membrane, and provides a pressure build-up necessary to expel the water through the less hydrophobic GDL pores into the cathode flow channels.
- (3) In addition, under long term operation it is reported that the presence of an MPL mitigates the loss of hydrophobicity in the macroporous diffusion media, possibly due to the enhanced liquid resistance [8].

An important aspect is the long term stability of the GDL since mechanical as well as chemical degradation has been observed. There are different methods reported for investigating aged GDLs [9]. GDL aging effects can be measured by enhanced lifetime tests and ex situ tests [10–15]. Enhanced aging tests at elevated temperatures or freeze–thaw cycles have been applied for in situ aging, whereas exposure to aggressive media, e.g., oxidative ambient conditions with hydrogen peroxide solutions are used for ex situ aging [10–13].

Atomic force microscopy (AFM) techniques have proven to be a valuable tool for the investigation of fuel cell components since

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their properties are dependent to a large extent on their nano-structure. With AFM the surface topography as well as different properties such as i.e. conductivity, adhesion force, elasticity, and dissipation energy can be measured and statistically analyzed [16–18]. Two main reasons for degradation of the PEMFC GDL are known, namely changes of GDL wetting behavior and GDL structural changes. Change of wetting behavior is induced by PTFE decomposition or depletion, mechanical abrasion or impurities. The loss of hydrophobic surface properties results in an accumulation of liquid water in the GDL pores and leads to a blocking of these pores for reactant transport. Changes of the structure of the GDL are caused by mechanical compression and wear. As a result of these changes water transport in the pores is modified and different electronic as well as heat conductivity is observed. Chemical decomposition of GDLs by carbon oxidation has been discussed but its importance as degradation mechanism is presently largely unclear.

This investigation explores the possibilities of using AFM techniques for detecting aging of fuel cell components on the nano-scale but does not intend to deduce new degradation mechanisms. The potential and limits of AFM investigations are evaluated for fuel cell degradation and compared with infrared spectroscopy results. The novel material sensitive AFM is explored for the investigation of MPL material degradation after operation and under accelerated degradation conditions. In order to correlate local properties an experiment with a segmented fuel cell is also used to detect differences between highly interface sensitive AFM and bulk sensitive infrared spectroscopy. The latter method is shown to directly measure the PTFE content in the MPL and electrode. By preparation of sample with comparable composition and known different PTFE/carbon content the AFM measurement of PTFE content could be quantified to deliver relative PTFE contents.

2. Experimental

2.1. Methods

2.1.1. AFM Harmonix

The AFM measurements were performed with a commercial AFM system (Bruker Corp., Multimode 8). All images have been measured by the so called “HarmoniX” mode of the AFM [19–22]. With a specially formed asymmetric AFM tip the higher harmonic vibrations of the tip after contact to the sample are used to reconstruct the complete force–distance curve at every image point. Thereby the topography is measured together with images of the distribution of different surface and subsurface properties. In general, from a force–distance curve different properties can be retrieved, schematically demonstrated in Fig. 1. This force–distance curve has been measured on a commercial microporous layer. The elasticity (stiffness) is given by the slope $\Delta F/\Delta x$ of the retraction curve. After a defined travel path towards the sample the maximum force (peak force) at reversal point of the tip retraction is recorded. Due to deformation of the material mechanical energy is dissipated and results in a hysteresis of the path. The dissipated energy (work) is represented by the enclosed area between preceding and retracting branch of the force–distance curve. The adhesion force is the minimum force between sample surface and tip at the moment when the tip surface contact is lost. For recording quantitative data the magnitude of the different forces and the dissipated energy is calibrated before measurement. In this study, besides topography, adhesion forces and mainly the dissipated energy are analyzed in detail and were used as a relative measure for following the aging of fuel cell components. AFM images with 10 μm and 0.3 μm square sizes are recorded for this study. The relative frequency of occurrence of adhesion force and dissipation energy was calculated from

Fig. 1. Force–distance curve measured by AFM on commercial microporous layer of gas diffusion layer with evaluated properties.

all recorded images, displayed as histogram and the peak values of every image evaluated and the data of all images were statistically evaluated. In Fig. 2a the bimodal distribution of energy dissipation on a commercial MPL is shown. For a sufficient confidence level a mean value (including error bars for one standard deviation) is calculated from several images measured under the same conditions. Most of the AFM measurements have been performed under ambient conditions at room temperature and a relative humidity (RH) of about 30–40 % (labeled as “dry”). Some measurements (labeled as “wet”) have been performed after rinsing the sample in ultra pure water (Millipore) and after carefully removing excess liquid water with water absorbent paper. An example of different surface properties measured simultaneously on a commercial MPL surface is presented in Fig. 3a–e as 3D-views. The topography of 1 μm^2 area (Fig. 3a) and an overlay of the phase shift onto the topography (Fig. 3b) are shown. In the phase shift image different materials which cause a different damping of the tip oscillation can be discerned. In Fig. 3c the adhesion force is overlayed with the topography, whereas in Fig. 3d the energy dissipation, and in Fig. 3e the hardness calculated as DMT modulus are used as overlays of the topography image. In the Fig. 3b–d the distribution of hydrophilic and hydrophobic as well as hard and soft surface components is clearly observable.

Fig. 2. Histogram of energy dissipation of single AFM image on MPL.

Fig. 3. (a) Topographical image of a MPL as 3-dimensional view, imaged by AFM of size $(1 \times 1) \mu\text{m}^2$. (b) Topographical image of a MPL from (a) with an overlay of the phase shift imaged by AFM of size $(1 \times 1) \mu\text{m}^2$. (c) Topographical image of a MPL from (a) with an overlay of adhesion force imaged by AFM of size $(1 \times 1) \mu\text{m}^2$. (d) Topographical image of a MPL from (a) with an overlay of energy dissipation imaged by AFM of size $(1 \times 1) \mu\text{m}^2$. (e) Topographical image of a MPL from (a) with an overlay of DMT modulus imaged by AFM of size $(1 \times 1) \mu\text{m}^2$.

2.1.2. Infrared spectroscopy

Fourier-transform infrared (FT-IR) spectra (ATR technique) of the samples cut according to their segment size from the fuel cell were

recorded using a platinum coated ATR unit with a germanium crystal. The spectra were performed on a Bruker Vertex 80v spectrometer (Bruker Optik GmbH, Ettlingen) with a resolution of 2 cm^{-1} and a

base pressure of 2 hPa in the sample chamber. The measurements were performed under vacuum conditions to exclude interfering vibration bands of CO₂ and H₂O. The analysis gives a mean value of an area of about 1 mm in diameter. Peak analysis of the C–F vibrations is performed using OPUS software (Version 6.5 from Bruker Optik GmbH, 2009) in order to determine the absolute peak intensities. The quantitative analysis is standardized with a linear baseline from 1262 and 1078 cm^{−1} (inset in Fig. 14). The area above this baseline was calculated for every spectrum individually. The absolute intensities are shown in Figs. 14 and 15. They represent a relative measure for the amount of PTFE in the analyzed volume. These values have been correlated with AFM data.

It should be noted that the information depth of AFM and infrared spectroscopy measurements is quite different. According to Table 1 with both analysis methods only a fraction of the GDL or electrode volume can be analyzed by both methods, whereby the AFM measurements deliver the properties of the interface only and IR probes a fraction of the volume beneath the surface. A comparison of the results from both methods at exactly the same area will always be a comparison of different sample volumes. The different parts of the sample may be affected by distinct aging or are already different due to preparation or contamination.

2.2. Experiments

2.2.1. Microporous layers (MPLs) of gas diffusion layers (GDLs)

The investigated commercial GDLs were operated in a single fuel cell test station in a normal configuration for different operation durations. The membrane electrode assemblies (MEAs) used were Ion Power Inc. catalyst coated membranes (CCMs) consisting of Nafion NR-111 membranes with SGL Sigracet 35 DC and SGL Sigracet 25 BC as GDL. The measurement with Sigracet 35 DC was performed at 80 °C, at a current density of 0.5 A/cm², and a pressure of 1.5×10^5 Pa for H₂ with a stoichiometric number of $\lambda = 1.5$ and relative humidity (RH) = 100 % at the anode. At the cathode the air was fed at ambient pressure with $\lambda = 1.5$ and RH = 50%. The cell with Sigracet 35 DC could only be operated for 12 h until a cell failure happened. A post mortem analysis by SEM revealed a hole in the MEA including the membrane. The cell equipped with the GDL Sigracet 25 BC showed only gradual degradation and was operated for 650 h at 60 °C, at a mean current density of 600 mA/cm² (area 100 cm²), $\lambda_{H_2} = 1.5$ at RH = 66%, and $\lambda_{air} = 2$ at RH = 42% at atmospheric pressure. After operation the GDLs were carefully removed from the MEA to keep the microporosity intact without transfer of MPL or electrode material to the other side of interface. After operation the components of the cell were carefully separated by hand. Scanning electron microscopy (SEM) inspection of the separated components exposed cohesive rupture of the MPL at the positions where the lands of the bipolar plates had put pressure onto the MEA. Therefore only the areas where a complete MPL or electrode is visible are analyzed by AFM. In Fig. 4 a typical material sensitive back scatter electron image shows the electrode with transferred material from the MPL (darker due to low proton number) pressed into the platinum containing electrode (brighter due to higher proton number). Another sample of SGL Sigracet 25 BC GDL was boiled in H₂O₂ for 1 h for accelerated artificial degradation.

Table 1
Thickness of investigated layers and information depths of infrared spectroscopy and evaluation of surface properties by atomic force microscopy.

	Thickness-/information depth/mm
Electrode	250
Microporous layer	250
Infrared spectroscopy	5
AFM	0.005

2.2.2. Calibration and reference samples

For calibrating the adhesion force and the energy dissipation a series of porous conducting samples was prepared containing carbon ENSACO 250G and PTFE with different known content of 40%, 60%, and 80% PTFE, respectively. The evaluated data of these samples were measured by HarmoniX mode and their properties were evaluated as described above and displayed in Fig. 5. From the slope of the adhesion force a change of 5.2 nN per % PTFE loss ($R^2 = 0.9997$) and for the energy dissipation a slope of 1.0 meV per % PTFE loss ($R^2 = 0.9231$) was calculated. This measurement demonstrates the effectiveness of material sensitive AFM to distinguish two components at the surface. As further reference samples representing the two pure phases in the MPL a Teflon sheet and a hand pressed carbon black pellet from ENSACO 250 powder were prepared and investigated by AFM together with the aged MPL samples and an unused MPL of the same type. All investigations were performed with the same AFM tip.

2.2.3. Segmented cell

In order to locally measure current–voltage curves during operation the anode flow field of a single cell is divided into 16 segments. At the anode a so-called chocolate wafer flow field with small segments of 1×1 mm² area separated by a space of 1 mm [23,24] and as cathode flow field a single serpentine has been used. Land and channel dimensions are 1 mm each. A view of the segmented anode flow field is given in Fig. 6 together with the labeling of the segments. The hydrogen gas was fed at position 1 with an outlet at segment 16, air inlet was situated at segment 16 with the outlet at segment 1. The single fuel cell was equipped with an Ion Power Inc. CCM, an ETEK single-sided GDL at anode, and a SGL 25 BC GDL at cathode. It was operated for 350 h at $T = 80$ °C, and an over pressure of 1.5×10^5 Pa for H₂ ($\dot{V}_{H_2} = 157.5$ ml/min, $T_{humidifier} = 70$ °C) and air ($\dot{V}_{air} = 525$ ml/min, $T_{humidifier} = 70$ °C). The current density of the 16 segments is set to a fixed value of 384 mA/cm² during the measurement. Segments 1, 6, 11, and 16 in the diagonal and segments 13, 14, 15, and 16 in the bottom row were analyzed by AFM. All 16 segments were investigated by infrared spectroscopy to determine the PTFE content.

3. Results and discussion

3.1. Microporous layers

The measurement of surface properties by AFM HarmoniX mode delivers material sensitive information of the surface but no direct

Fig. 4. Scanning electron microscopy image of electrode area after disassembling, dark area marks transferred carbon material from MPL at position of flow field lands.

Fig. 5. Calibration of PTFE loss by AFM measurement of adhesion force and energy dissipation with topography of a sample with 80% PTFE content and energy dissipation of samples with 40% and 80% PTFE content, respectively, size $(3 \times 3) \mu\text{m}^2$.

Fig. 6. Used cell with segmented flow field (left) and labeling of the segments (right).

chemical information of the different discernable phases. This information needs to be retrieved from a comparison of the different measured properties together with the knowledge of the components of the sample. The change of adhesion force and energy dissipation of PTFE/carbon samples has been calibrated by AFM analysis of samples with known composition. The properties of the aged samples after operation were measured and compared to those of the unused samples before operation and the relative change of composition could be retrieved and quantified using the calibration data. In addition, samples prepared with the pure materials were measured as reference for the properties of the pure phases. In Fig. 7 AFM images of the adhesion force on $1 \mu\text{m}^2$ area on MPL Sigracet 35 DC are displayed all with the same data scale of 200 nN. The image on the left measured under dry conditions on an unused MPL shows the distribution of adhesion force. In the middle the adhesion force at the anode after 12 h of operation exhibits areas with very low adhesion (dark areas) if measured under dry conditions. If measured wet (image on the right) the adhesion force has largely increased overall on the surface. A high value of adhesion force is an indication for high molecular forces between AFM tip and surface. In this study the adhesion force between a PTFE surface and the AFM tip was found to be significantly higher compared to carbon. The darker area, which can therefore be interpreted as carbon surfaces without PTFE layer, has increased significantly after operation and indicates a loss of PTFE. This

interpretation is validated by the results of the measurement on a wet surface. The whole measured wet surface exhibits a homogeneously distributed increased adhesion force (bright areas). The high adhesion force is due to water adhesion which is expected to be larger than the adhesion force between AFM tip and PTFE. Here also the surface areas were PTFE was initially (before operation) present can be wetted which leads to a higher adhesion compared to the value before operation.

Since the results from small surface areas may be misleading a statistical evaluation of AFM measurements has been performed and is given in Fig. 8. The mean values of adhesion force (Fig. 8a) and energy dissipation (Fig. 8b) are compared to the values retrieved at a solid PTFE sample and a hand-pressed carbon pellet measured under the same (dry) conditions. The comparison of data before and after operation reveals an overall decrease of both properties after operation and was found to be always larger at the cathode. The adhesion forces on the solid PTFE sample and the carbon pellet used as reference materials are higher compared to the mean values measured at the surface of the compound material of the MPL. Before operation the values of energy dissipation of the solid PTFE and the MPL are similar and are at variance with the value of the pressed carbon black sample which is significantly higher. The high value of energy dissipation measured at the latter sample is probably caused by its quite loose consistence (hand pressed) not comparable to the solid material of the MPL. The

Fig. 7. AFM images of GDL Sigracet 35 DC, imaged area $1 \mu\text{m}^2$, of adhesion force images at anode before and after operation measured under dry and wet conditions.

Fig. 8. Mean values of surface properties of MPL (Sigracet 35 DC) derived from AFM measurements under dry conditions from $1 \mu\text{m}^2$ area after 650 h operation. (a) Adhesion force. (b) Energy dissipation.

results of the statistical evaluation are consistent with the results from the adhesion force images of Fig. 7. An overall reduction of adhesion force and dissipation energy with regard to the reference PTFE sample is found, in this case larger at the cathode than at the anode. Using the values measured by calibration the reduction of PTFE content was about 0.5% at the anode and 1% at the cathode.

In Fig. 9a and b the change of adhesion force and energy dissipation measured at the MPL of two differently operated fuel cells is compared. One cell has been operated for 650 h and the other for only 12 h, but with an evolving hole in the MEA. Adhesion force and energy dissipation decrease with operation in both cases, again the effect is stronger at the cathode than at the anode. Despite the short operation time of 12 h the decrease of adhesion force and energy dissipation is much larger for this sample compared to the cell normally operated for 650 h. According to the calibration data there is a loss of PTFE of almost 2% at the cathode. The hole found in this MEA during post mortem analysis by SEM caused a significant hydrogen as well as oxygen crossover in the cell leading to accelerated thermal and chemical degradation which could explain its short life time and accelerated degradation of the material composition. A comparable decrease of material properties is visible after artificial degradation of 1 h treatment with H_2O_2 . It has been

shown above that the decrease of adhesion force and energy dissipation measured under dry conditions is indicative for a loss of PTFE. This interpretation is again supported by the results of similar statistically evaluated measurements on the MPL of Sigracet 25 BC measured wetted with water. In Fig. 9c the results of adhesion force measured dry and wet are compared for the cell operated for 650 h. Now the adhesion force before operation has the lowest and at cathode has the highest values. Following the above argumentation, a larger surface area is hydrophilic on the cathode compared to the anode due to an increased removal of PTFE. The loss of hydrophobic surface leads to higher water coverage and thereby to a stronger adhesion force. It can also be concluded that the adhesion force due to water adhesion is larger than the adhesion force to PTFE, represented by the data retrieved at solid PTFE.

The results validate the usability of adhesion force and energy dissipation measured by AFM as a measure for PTFE loss of a MPL. A more severe degradation of the cathode side can be deduced for both experiments as discussed before [18].

3.2. Segmented cell

As a further experiment in order to explore the possibilities and limits of AFM investigation, a segmented cell [25,26] was analyzed after operation by AFM HarmoniX mode and by infrared spectroscopy (IR). With IR the PTFE content can be analyzed up to a depth of several micrometers and was compared to the results of AFM experiments for the surface of the same segment.

Fig. 10 visualizes the change of cell potential of the 16 segments at five different operation times during operation with a fixed current density. In the first 50 h the potential distribution changes dramatically according to the activation of the cell. Thereafter an overall decrease of the potential of all segments without further significant changes of the relative magnitude of current density is observed. After disassembling the cell the MPL side of the GDLs as well as the electrodes was analyzed. Only the segments of the diagonal and the last row of the cell at the cathode side for both sides of the interface were analyzed by AFM. With infrared spectroscopy the PTFE content of both sides of the interface, MPL and electrode, of all segments at cathode and anode was investigated using the C–F vibrational signatures. Fig. 11 gives a schematic overview of the assembly of this cell as well as the labeling of the investigated interfaces.

The two techniques used for analysis deliver different information of the samples. AFM gives information on the surface properties of a sample with high spatial resolution; in case of adhesion force the properties of only the first molecular layer is probed. In case of energy dissipation the information depth measures a few

Fig. 9. Comparison of MPLs (Sigracet 35 DC and Sigracet 25 BC) after fuel cell operation, artificially degraded (Sigracet 25 DC), and solid PTFE derived from AFM measurements under dry conditions as mean values from 1 μm^2 area. (a) Adhesion force measured under dry conditions. (b) Energy dissipation (dry). (c) Adhesion force measured under wet conditions.

Fig. 10. Change of local potential of segmented cell during constant load at 384 mA cm⁻².

Fig. 11. Schematic cross section of segmented cell with analyzed interfaces.

nano-meters because the AFM tip puts pressure onto the surface to probe the deformation of the interface. Therefore the adhesion force is indicative of the properties of a very thin surface layer or even a contamination layer; the energy dissipation is indicative

for mechanical properties with a depth of a few nano-meters. In both cases only the interface is investigated. With infrared spectroscopy molecular vibrations can be probed up to several micrometers inside the solid volume underneath the surface. Therefore the PTFE content derived from the vibration of the C–F band gives information on the PTFE content of a comparably thick layer, although this layer represents also only a fraction of the whole sample. In practical terms, the relative change of PTFE from AFM is indicative for properties of interface whereas IR probes the bulk material. For both methods relative changes need to be compared to a reference sample to get quantitative data. The unused fuel cell is taken as the reference. Note that the electrodes of the cell are the same on anode and cathode but the cell contains different GDL/MPL layers at anode and cathode due to cell operation requirements. The homogeneity of both MPL materials has been measured by infrared spectroscopy on unused samples. The standard deviation of PTFE content across the area of an unused SGL Sigracet 25

BC was determined to be 8% and of an unused ETEK MPL to be 6%. The scattering of PTFE content is comparably small and therefore the reported changes in the samples in Figs. 14 and 15 are indicative of differences caused by operation. As has been demonstrated a decrease of adhesion force and energy dissipation is indicative of PTFE loss. The disassembling of the cell after operation causes some material transfer as detected by SEM, but nevertheless it was possible to find intact surface areas for analysis. This can be proven by comparison of adhesion force, which is very sensitive to contamination of the surface and energy dissipation. As it is shown in Fig. 12a at the cathode electrode interface both data behave in parallel and no severe contamination is assumed to be present.

In Fig. 13 the surface topography together with the surface properties of the MPL of segment 16 (GDL SGL 25 BC) measured by HarmoniX-mode is displayed. In the topography image (Fig. 13a) carbon particles attached to PTFE filaments are visible. In the phase shift image (Fig. 13b) a different energy loss for different filaments can be seen, in particular bright filaments in the middle of the image and dark ones on the bottom are observed. The phase shift is caused by all forces acting on the tip and the similarity with the adhesion force image (Fig. 11c) indicates the dominance of adhesion in the energy loss. An interesting observation is the presence of bright and dark filaments in the material sensitive images. These filaments with a reduced (dark area) adhesion also are comparably soft as deduced from the peak force image (Fig. 13d, dark areas). In the original MPL structure only PTFE filaments are present and it is concluded that these changes are caused by the fuel cell operation where degradation is accompanied by a decreased adhesion of the carbon/PTFE.

In Fig. 12a the mean adhesion force for the segments investigated by AFM at cathode MPL is compared with the energy dissipation. Both signals exhibit a similar trend along the segments. A parallel change of adhesion force and dissipation energy has also been measured above during analysis of MPL layers and is demonstrated to be a measure for the PTFE content in this material. In Fig. 12b the energy dissipation of anode and cathode MPL is compared for the same segments. Even though the gas diffusion media

at anode and cathode are of different nature from two suppliers, the energy dissipation of gas inlet (1) and outlet (16) and those of segments 14–16 of the last row close to the outlet have a comparable value. A large difference, more precisely an almost anti-parallel behavior, is visible in the other segments analyzed by AFM (diagonal of fuel cell). Whereas at the cathode high values (less aging) are visible in segments 11 and 13 associated with a high PTFE content, at the anode side a minimum (low PTFE content) is measured at segment 11. Obviously a different aging process of anode and cathode MPL has to be assumed for these segments during fuel cell operation. Close to the hydrogen inlet and along the diagonal segments in direction of hydrogen pressure gradient a larger decrease of PTFE is found at the anode side, whereas near the air inlet no significant differences are visible between anode and cathode. The different magnitudes of PTFE and thereby of aging processes may be caused by local differences in fuel supply.

In contrast to the results of AFM measurement, where only the properties of the very surface are probed, IR provides information from a layer of several micrometer thickness and measures the PTFE content inside the bulk. The inset in Fig. 14 illustrates the evaluation of the PTFE content from the IR spectrum. In Fig. 14a the results of energy dissipation measurements for anode and in 14b for cathode MPL are compared to the relative PTFE content derived from IR measurements at the same segment. There are some similarities in the overall trend of IR and AFM results for the displayed segments, but at anode side the maximum values are found in different segments and at cathode side there are almost no differences in PTFE content from IR besides a sharp maximum in segment 11 in contrast to the values of energy dissipation. In the previous chapter the relative changes of dissipation energy have been shown to be a measure for the PTFE content. The differences visible in Fig. 14 may be explained by the different sampling depth of the two methods and probably reflect differences in PTFE content between material at the interface and inside the MPL layer. Reasons for these differences cannot be substantiated in this case, but in general at the interface in addition to the chemical degradation the influence of an enhanced mechanical stress is present which may be responsible for this changes.

Fig. 12. (a) Mean values of adhesion force and energy dissipation measured by AFM at cathode MPL at different segments. (b) Comparison of mean values of dissipation energy measured by AFM at cathode and anode MPL.

Fig. 13. AFM images of cathode MPL (segment 16). (a) Topography of imaged area of $3 \mu\text{m}^2$. (b) Phase shift of tip oscillation corresponding to total energy loss. (c) Adhesion force. (d) Peak force at tip reversal point.

In Fig. 15 the relative PTFE content from IR and AFM (energy dissipation) measurements of the cathode electrode is compared to the voltage loss over 100 h of cell operation of segments 10–16 (if measured for this segment, note that some samples were not reliable due to material transfer). One should note that the voltage loss differences between the segments are not very high. Since at the fixed current density these voltages are in a range of the current–voltage curve (380 mA cm^{-2}) were already the mass transport plays a significant role an influence of the PTFE content/hydrophobicity on the voltage loss of the cell could be expected. There is no general correlation between a higher voltage loss and a low PTFE content at the electrode. The PTFE content at the interface of the last row (segments 13–16), represented by the energy dissipation values, is almost parallel to the voltage loss. A higher dissipation value is correlated to a higher PTFE content and correlated here to a smaller voltage loss. No correlation is found with the IR intensity, which is representing the PTFE content beneath the surface.

The PTFE content as derived by IR for all segments of the cell area and all four interfaces is given in Fig. 16 together with the local mechanical pressure measured by introducing a pressure sensitive paper instead of the MEA between the GDLs. Small relative differences in PTFE content over the whole cell area are found for

the cathode MPL (Fig. 16c), whereas the relative differences are larger across the cathode electrode (Fig. 16a). In the anode MPL (Fig. 16d) a large reduction of PTFE is found in a few segments, at the anode electrode (Fig. 16b) a larger general reduction but with a similar distribution is measured. A serpentine flow field at cathode is expected to homogeneously distribute the air, whereas at the anode the hydrogen is flowing in direction of the pressure gradient from gas inlet at segment 1 to the outlet at segment 16. The distribution of fuel is obviously influenced by the geometry, more precisely by the local compression and impression of the GDL into the channel. This GDL impression is modulated by the mechanical pressure distribution of the different segments. To some extent a correlation of the degree of local reduction of PTFE content with the local pressure is observed. Taking this into account, the local differences in PTFE content and degradation may mirror the local concentration of fuel. For example, at segment 11 a high mechanical pressure of the anode flow field into the GDL may lead to geometric constrictions and a lower local hydrogen supply. It is known from the literature, that fuel starvation can cause higher degradation at the anode [26].

Although in this study an unambiguous causality between local fuel supply and degree of degradation cannot be demonstrated

Fig. 14. Comparison of mean values of energy dissipation with IR intensity at (a) anode MPL and (b) cathode MPL; inset on the right illustrates the evaluation of IR intensity from the C–F vibration band.

Fig. 15. Comparison of segment voltage loss with IR intensity and mean values of dissipation energy at cathode electrode.

Fig. 16. PTFE content from IR intensity of all segments at (a) cathode electrode, (b) anode electrode, (c) cathode MPL, (d) anode MPL and the contact pressure distribution (segment flow field on MEA) across the cell area in the center of figure.

there are some trends which support this interpretation. In general, the smallest overall PTFE content is measured at the cathode electrode. A higher degradation of the cathode electrode material which then causes a reduction of output power is also often found in literature [27].

4. Conclusion

It could be demonstrated that the relative change of energy dissipation and adhesion force measured by AFM HarmoniX mode (Bruker Corporation) can be used as a measure for the PTFE content to follow aging of MPLs due to fuel cell operation. Quantitative values for PTFE loss could be retrieved by calibration of measured data from MPL surfaces with data retrieved on samples with comparable composition and known different PTFE content. The analysis of differently operated MPLs was used to identify differences in degradation between cathode and anode MPLs. These effects were comparably large and were also evident for artificial aging with H_2O_2 . All measurements lead to the conclusion that the PTFE content at the surface of a MPL is reduced by fuel cell operation. The loss was in all cases larger at the cathode than at the anode. A very fast degradation was observed when a pin hole is present in the MEA. In this case, the loss of PTFE is as high as with exposure of the GDL to 1 h of H_2O_2 treatment.

A combination of AFM measurements, which are indicative of interface properties, with infrared spectroscopy, where the PTFE content can be measured with a larger penetration depth, can provide complementary information concerning the sampling depths and exhibit differences attributed to differences in aging between interface and bulk material. Large differences in PTFE reduction were found across the area of a segmented cell, in some parts stronger degradation was detected at the cathode and at other segments degradation was enhanced at the anode. Results of PTFE content of IR and AFM measured at the same MPL segments differed to some extent. This result is attributed to the differences in sampling depths. Although in the electrode a different composition compared to the MPL is present, a correlation of the measured magnitude of dissipation energy to the power loss was found and could be used to follow the degradation of electrode material as well.

The investigation indicates a correlation of the degree of degradation to the distribution of fuel across the area, and thereby the distribution of local power losses in this cell.

Due to the special design of this experimental cell the actual magnitude and distribution of degradation, however, cannot be generalized. In this study both techniques, IR and AFM, have proven to be complementary for an understanding of the aging processes during operation of a fuel cell, although a full explanation

of the cell behavior would need additional analysis, e.g., of the electrical properties by electrochemical impedance spectroscopy.

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