

# Synchrotron X-ray radioscopic in-situ study of high-temperature polymer electrolyte fuel cells – effect of operation conditions on structure of membrane

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## Keywords

synchrotron radiation; high-temperature polymer electrolyte fuel cell; phosphoric acid; in-situ radiography; imaging

## 1 Abstract

We present the first high-resolution synchrotron X-ray study on high temperature polymer electrolyte fuel cells (HT-PEFCs) in through-plane mode. Distribution and evolution of the phosphoric acid in the membrane electrode assembly was monitored in-situ/in-operando under different operating conditions at steady states. At current densities of  $350 \text{ mA cm}^{-2}$  and  $600 \text{ mA cm}^{-2}$  significant changes in local media distribution were detected mainly beneath the channels of the flow field. We assign this effect to a varying degree of acid doping over the active region. Furthermore it was found, that parts of the electrode structure were moved and partly irreversibly displaced after cell operation at load conditions. This effect might contribute to structural ageing of the electrodes.

## 2 Introduction

In recent years, much research was carried out to optimize the water management of low-temperature fuel cells [1, 2]. Non-destructive methods such as neutron or synchrotron X-ray imaging sometimes complemented by additional in-situ techniques, e.g. current density measurements, were successfully applied to study the influence of the water distribution on the performance of low temperature fuel cells [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. In contrast the water management of high-temperature fuel cells (HT-PEFCs) is directly linked to the equilibrium state of the phosphoric acid derivatives. However, adequate in-situ studies on variations in concentration and distribution of phosphoric acid are still rare [20, 21, 22]. Synchrotron imaging offers high spatial and temporal resolution and allows for in-situ analyses of dynamic transport processes. Compared to laboratory X-ray sources synchrotron sources provide enhanced beam intensity and quality and the opportunity to use monochromatic radiation [23,24]. For these reasons, synchrotron imaging is the most suitable approach for small-scale and non-destructive investigations of fuel cells and has, for instance, already been successfully applied to observe aging effects in HT-PEFCs [25, 26].

In contrast to low-temperature polymer electrolyte membrane (PEM) fuel cells, HT-PEFCs feature high carbon monoxide (CO) tolerance and can therefore be operated with low-purity gas (such as reformat gas). The proton conduction mechanisms within HT-PEFCs proceed by different reactions. These mechanisms are the Grotthus mechanism [27] and the PBI-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O conduction mechanism [28]. Thereby phosphoric acid reacts with water produced in the reactions and thereby forms equilibrium with the acids dehydration products (mainly pyro-phosphoric acid H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) [29, 30]. In the following, this water is referred to as 'product water'. Product water can also dilute the phosphoric. At operating temperatures around 160 °C one primarily expects two derivatives of phosphoric acid that occur in HT-PEFCs: ortho-phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and pyro-phosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>). Since hydration and dehydration of phosphoric acid results in a changing X-ray attenuation coefficient, the composition of phosphoric acid can be investigated in-situ by means of transmittance synchrotron X-ray imaging. This information is hardly accessible by any other measurement method due to the acidic environment present in HT-PEFCs.

In this study, HT-PEFCs were analyzed in-situ by means of synchrotron X-ray radiography. A dedicated test cell design was used in order to achieve high beam transmittance through the cell for both the through-plane (perpendicular to membrane layer) and in-plane (in parallel to membrane layer) perspectives. In addition to previous results [20] we achieved highly resolved spatial information about the distribution of phosphoric acid inside the membrane electrode assembly (MEA) in through-plane.

## 3 Experimental

### 3.1 Imaging setup

Radiography was performed with the tomography station at the BAMline (electron storage ring BESSY II of the Helmholtz-Zentrum Berlin)[31]. The synchrotron beam was monochromatized to 22 keV using a double multilayer monochromator with an energy resolution of about  $\Delta E/E = 1.5\%$  [32]. The detector system comprised a 20- $\mu\text{m}$  thick  $\text{CdWO}_4$  scintillator, a microscopic optic and a pco4000 camera [33] with a  $4008 \times 2672$  pixel<sup>2</sup> CCD chip that is kept out of the direct beam by using a mirror. With the settings chosen, each detector pixel corresponded to a sample area of  $2.15 \times 2.15 \mu\text{m}^2$ , while the temporal resolution was 8 s (6.5 s exposure time and 1.5 s read out time).

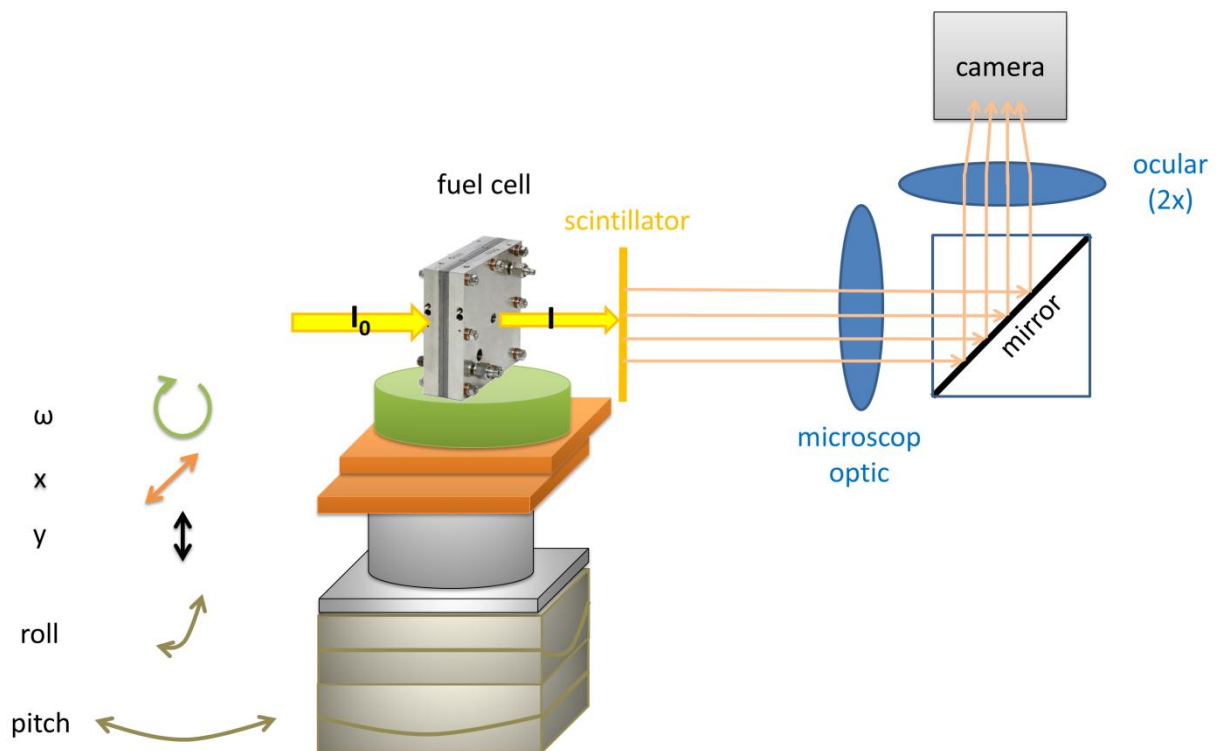
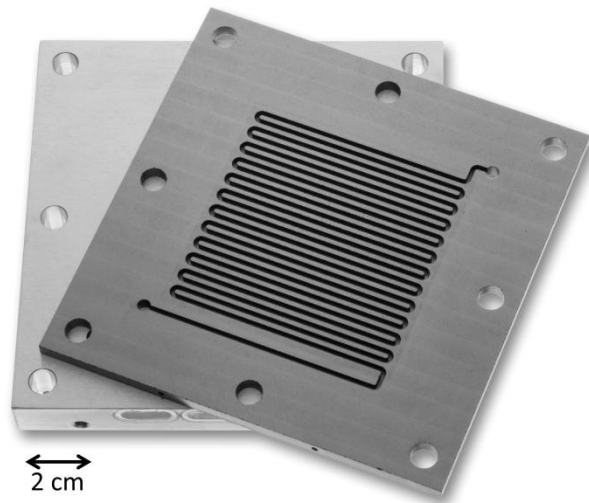


Figure 1: Experimental setup of the tomography station at BAMline (Helmholtz-Zentrum Berlin, Germany).

### 3.2 Fuel cells and MEA preparation

The cell design was specially developed for radiographic measurements by Forschungszentrum Jülich. The flow field was adapted in order to enhance beam intensity in the in-plane and through-plane orientations by drilling through-holes into the end plates thereby reducing the material thickness of the flow field plates. A single channel serpentine flow field geometry was used at the anode and

cathode sides, as shown in Figure 2. The channel depth was 2.5 mm; the widths of the channel and the rib were 1.5 mm. The active region was 49 cm<sup>2</sup> large.



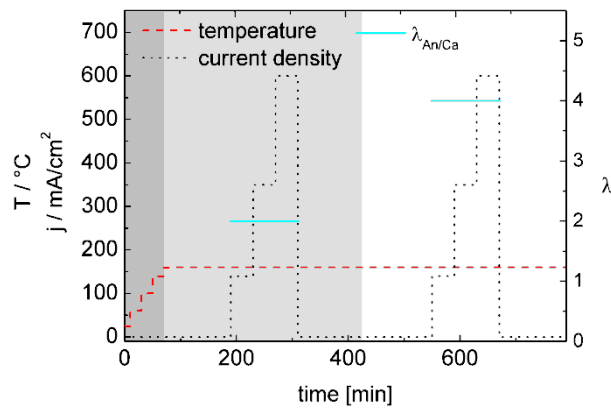
**Figure 2: Meandering single channel gas flow field geometry was used at the anode and cathode sides.**

Two identical cells were investigated in this study, referred to as HTT1 and HTT2 in the following. Prior to radiography, HTT1 was subjected to a break-in procedure at the Forschungszentrum Jülich, meaning that it was operated at a current density of  $j = 200 \text{ mA cm}^{-2}$  for 70 h in a test rig. Subsequently, it was shut down and transferred into a mobile test rig in order to perform radiography and impedance spectroscopy at BESSY II. No such break-in procedure was performed for test cell HTT2. This cell was assembled on-site just 2 h prior to radiography.

A commercially available gas diffusion layer (GDL) composed of non-woven carbon fibers with a micro porous layer on one side (H2315 C2, Freudenberg FCCT KG) was coated with a dispersion of carbon-supported catalyst (20 % HP Pt on Vulcan XC-72, BASF Fuel Cell, Inc.), PTFE (Dyneon, 40 wt% in the final catalyst layer) and dispersants applying the doctor blade technique. The gas diffusion electrodes (GDE) were produced with a platinum loading of  $\sim 1 \text{ mg cm}^{-2}$ . After drying at room temperature, the anodic and the cathodic catalyst layers were each doped with  $20 \text{ mg cm}^{-2}$  phosphoric acid using a solution of ethanol : 85% aqueous phosphoric acid (4 : 1 w/w). This solution was pipetted dropwise as a quadratic grid over the whole electrode area until the final doping level had been reached (see also [34]). After this, the GDEs were joined with a 30- $\mu\text{m}$  thick undoped poly(2,5-benzimidazole) (ABPBI) membrane (FuMA-Tech GmbH) in a test cell without preceding hot-pressing.

The cells were heated up stepwise at ambient pressure to approach the operating temperature of 160 °C, see Figure 3. For all the experiments, dry gases were supplied and the flow rates of hydrogen

and air at current densities equal to or greater than  $j = 140 \text{ mA cm}^{-2}$  were adjusted to meet the stoichiometric rates of  $\lambda_{\text{An/Ca}} = 2/2$  or  $4/4$ , respectively. At open circuit voltage (OCV) the flow rates were kept equivalent to  $\lambda_{\text{An/Ca}} = 2/2$  at  $j = 140 \text{ mA cm}^{-2}$  for the duration of 2 hours. After the operation at OCV the cells were operated at increasing current densities ( $140 \text{ mA cm}^{-2}$ ,  $350 \text{ mA cm}^{-2}$  and  $600 \text{ mA cm}^{-2}$ ) at stoichiometric rates of  $\lambda_{\text{An/Ca}} = 2/2$  and  $\lambda_{\text{An/Ca}} = 4/4$ , see figure 3. The current densities were kept constant for 40 min to achieve steady state conditions inside the MEA. After this, the cells were operated under OCV for 2 h again. Radiographs were continuously taken throughout the entire experiment.

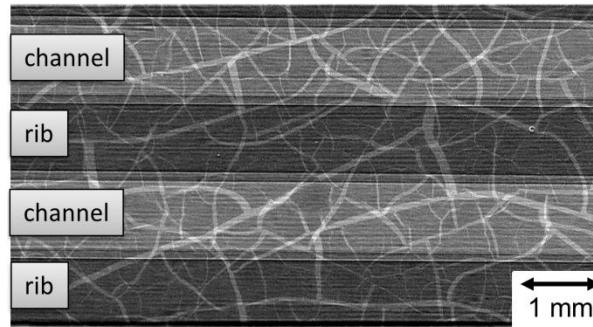


**Figure 3: Sketch of the measuring procedure which shows three parts. Dark gray rectangle represents the heating up, following by two almost identical programs (first program was run with a stoichiometry of  $\lambda_{\text{An/Ca}} = 2/2$  while  $\lambda_{\text{An/Ca}} = 4/4$  was used for second program) which are marked by gray and light gray rectangles respectively. Both programs were run starting at open circuit voltage (OCV) for 2 h, followed by operating conditions at different current densities for about 40 min.**

## 4 Results

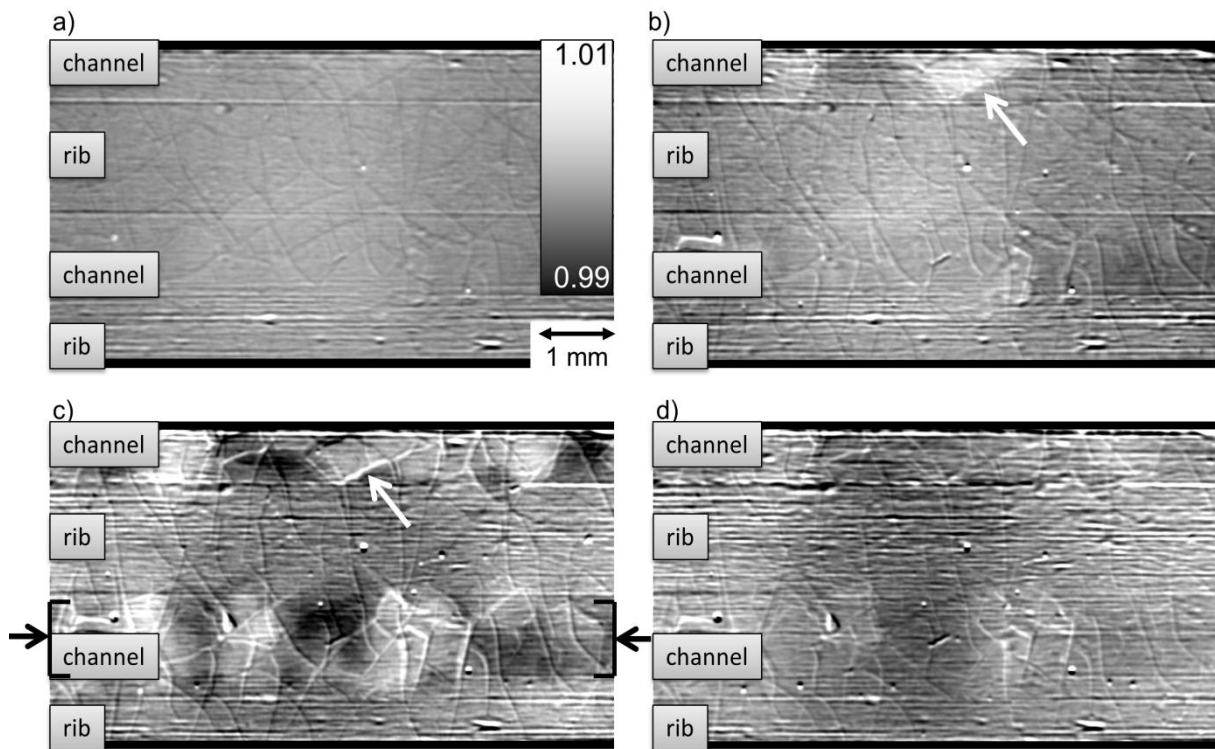
Through-plane radiographs were taken from the center of the active region where all the channels are parallel to each other and are arranged horizontally, see Figure 2. The dominating features of cell HTT1 as shown in Figure 4 is the regular channel-rib pattern of the flow fields and the irregular pattern of cracks within the catalyst layers which originates from a fabrication step of the electrodes. The anodic and cathodic flow fields are aligned with only little overlap, visible by the double structure of the channel edges. The reason for the overlap ( $107 \mu\text{m}$  for cell HTT1 and  $12 \mu\text{m}$  for cell HTT2) is a mismatch of anode sided and cathode sided flow field in the projection which occurred during cell construction. Since the mismatch is small compared to the flow field dimension this does not affect the operation significantly. The electrodes have a fragmented appearance on both the anode and the cathode side. The cracks in the electrodes are narrower underneath the ribs compared to those

underneath channel areas. This is caused the compressing of the cell which also compresses the fragments of the electrodes.



**Figure 4: Through-plane perspective of center part of cell HTT1 (flat- and darkfield-corrected radiograph). Flow field channels show up as bright areas, whereas the ribs appear dark. The anodic and cathodic flow field patterns show a slight vertical mismatch (for descriptions please see text above).**

The series of normalized images in figure 5 represents the changes in transmittance of cell HTT1 (for the same image section as shown in Figure 4) at different current densities but at constant stoichiometries  $\lambda_{An/Ca} = 2/2$ . The radiographs were normalized with respect to a radiograph taken after OCV had been applied for 2 h. Light gray values ( $> 1$ ) indicate an increase of transmittance under load conditions while darker values ( $< 1$ ) indicate lower transmittance. At a current density of  $140 \text{ mA cm}^{-2}$  (figure 5a) no significant change of transmittance was detectable. Upon increasing the current density to  $350 \text{ mA cm}^{-2}$  (figure 5b) local changes of the transmittance showed up and intensified after the current density had further been increased to  $600 \text{ mA cm}^{-2}$  (figure 5c). The images in figure 5 reveal a change (increase and decrease) in the local transmittance of up to 1% especially beneath the channel areas (see figure 5c). These changes can be assigned either to a changed distribution of the liquid media or alternatively to inhomogenous swelling of the membrane (see below). Furthermore, bright white stripes at the edges of the electrode fragments become visible. They are caused by movement of the electrode fragments or by changes of their shapes. These two different kinds of transmittance changes will be separately investigated.



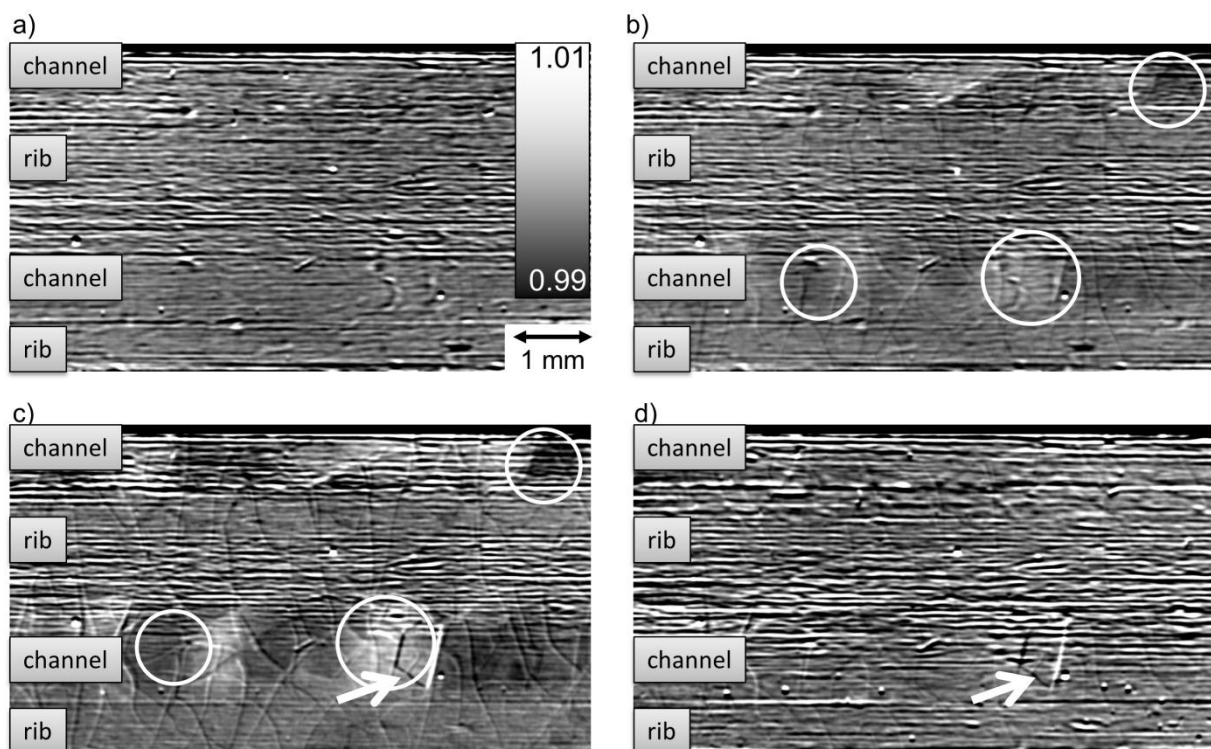
**Figure 5: Cell HTT1 operated at different current densities (1-fold serpentine flow field, 160 °C,  $\lambda = 2/2$ ) normalized to the operation condition after 2 h at OCV. a) 140 mA cm<sup>-2</sup>, b) 350 mA cm<sup>-2</sup>, c) 600 mA cm<sup>-2</sup>, d) 0 mA cm<sup>-2</sup> (OCV). In order to achieve steady state conditions, only radiographs taken at the end of each operating condition were chosen. Gray values show the changes of normalized transmittances between 0.99 (black) and 1.01 (white). The region shown is the same as in figure 4.**

Changes within channel areas are more pronounced than those of rib areas. Note that the scale of transmittance variation during the measurement is small (a few tenths of a percent). In order to visualize the differences, strong contrast enhancement was performed in figures 5-7, which, however, also gave rise to artifacts such as horizontal streaks and bright spots which are produced by the monochromator and scintillator defects.

The dimension of individual areas affected by a positive or negative change in transmittance in Figure 5 is in the same range as the width of the channels and broader than maximum electrode fragments dimensions. These areas form an almost periodical pattern with a period of around 1 mm. Furthermore the sharp transmittance changes at the electrode fragment edges seem to be somehow correlated to this periodical structure, i.e. they appear mainly in areas with strong overall changes in the transmittance. In some cases a correlation between the individual shape of an electrode fragment and that of the zone with altered transmittance can be found. This is quite obvious at the top of figure 5b and c (marked by white arrows) where the outer edges of fragments perfectly match with the borders of areas with a changed transmittance.

It is interesting to remark that the overall periodic structure remains unchanged for different load conditions as exemplarily shown in Figure 6b and c (indicated by white circles). Furthermore the structure is reproducible after restart of the cell. Locations of maxima and minima of the structures in figures 5c and 6c are almost identical (note: Radiographs in figures 5 and 6 are taken from the same location in the cell, see above). The electrode fragments change their locations by a few microns (see white arrow in Figure 6c and d). Figure 5d indicates that after about 2 h of cell operation at OCV local transmittance changes are still present. Apparently, the operation at non-zero current densities induced irreversible changes of the cell structure.

In a further experiment the current density was again increased in discrete steps, this time at increased stoichiometry of  $\lambda_{An/Ca} = 4/4$ . Figure 6 shows the resulting changes of the transmittances which are less pronounced than those observed at lower stoichiometries.

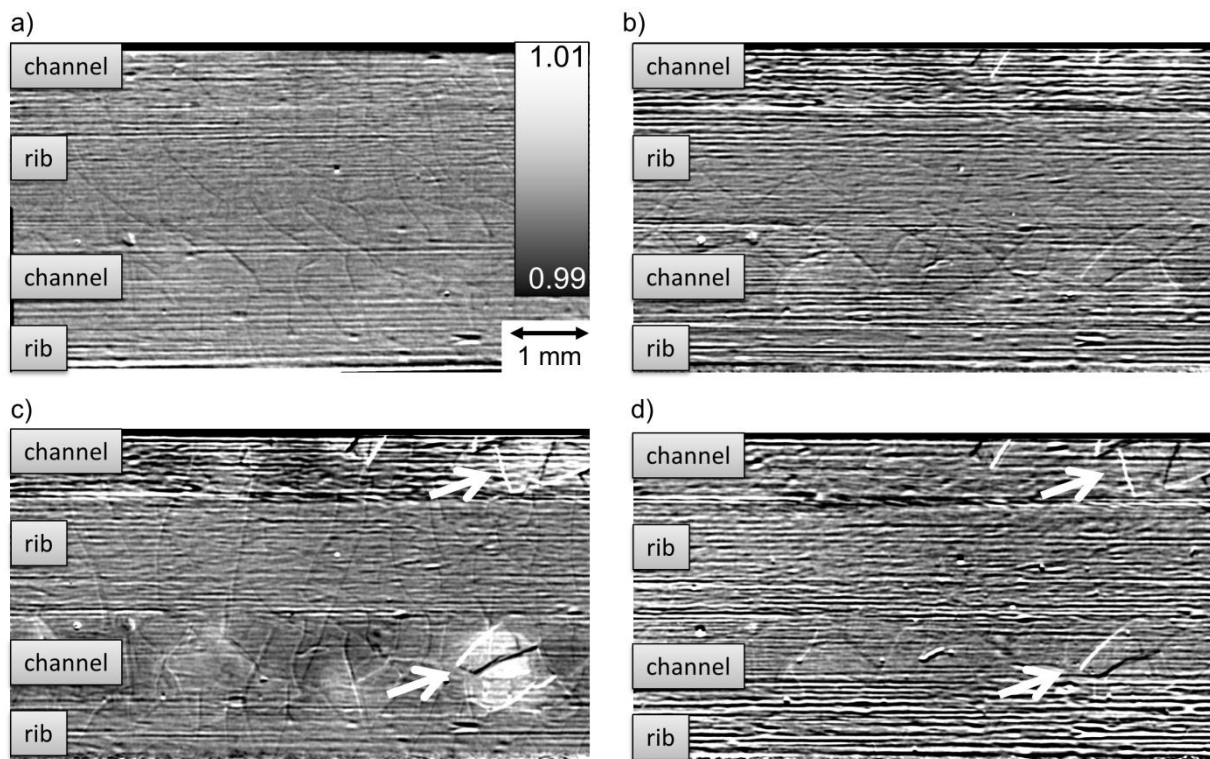


**Figure 6: Cell HTT1 operated at different current densities (1-fold serpentine flow field, 160 °C,  $\lambda = 4/4$ ) normalized to the operating condition after 2 h at OCV. a) 140 mA cm<sup>-2</sup>, b) 350 mA cm<sup>-2</sup>, c) 600 mA cm<sup>-2</sup>, d) 0 mA cm<sup>-2</sup> (OCV). Gray values show the changes of normalized transmittances between 0.99 (black) and 1.01 (white). The region shown is the same as in figure 4.**

Figure 7 shows the development in cell HTT2 during the stepwise increase of current density at a stoichiometry of  $\lambda_{An/Ca} = 2/2$ . Changes of transmittance and fragment movements are very similar to those observed for cell HTT1 at  $\lambda_{An/Ca} = 2/2$ . Again, the local changes of transmittance and the dislocation of fragments are most pronounced beneath the channel regions. Overall, the fragment

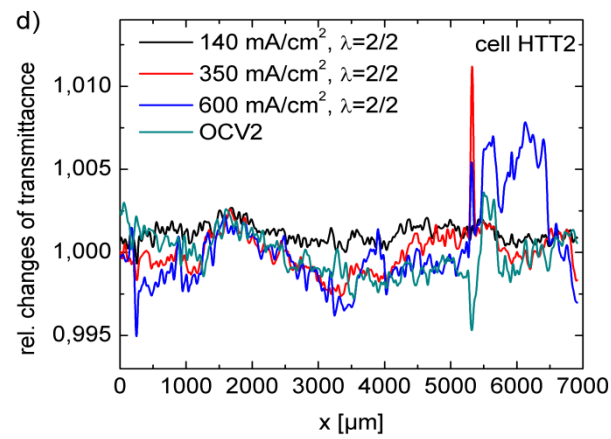
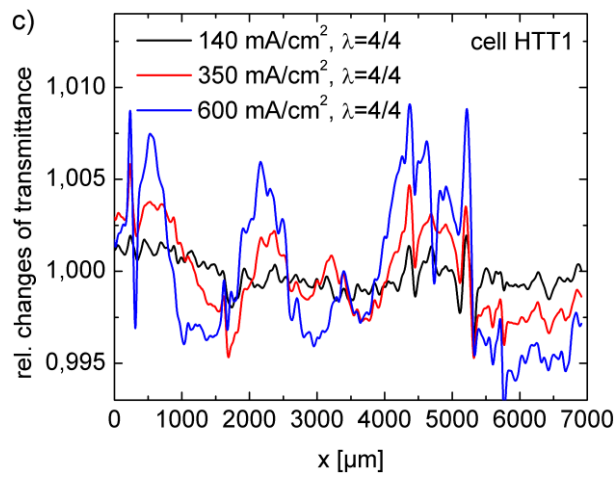
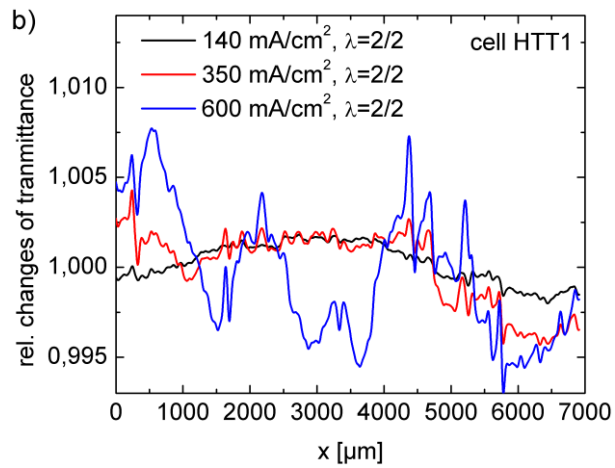
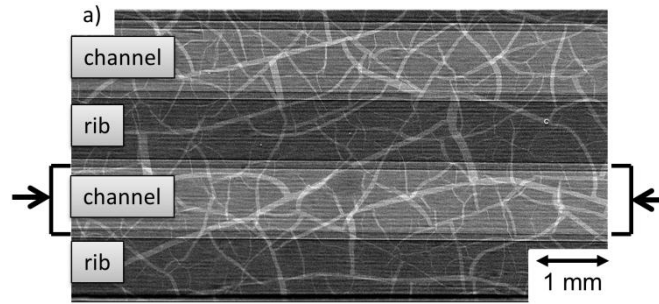


displacement appears to be stronger in cell HTT2 than in cell HTT1. Especially in regions of large transmittance changes, fragment displacements are not totally restored. Some of these locations are marked by white arrows in figure 7c and figure 7d.



**Figure 7: Cell HTT2 operated at different current densities (1-fold serpentine flow field, 160 °C,  $\lambda = 2/2$ ) normalized to the operating condition after 2 h at OCV. a) 140 mA cm<sup>-2</sup>, b) 350 mA cm<sup>-2</sup>, c) 600 mA cm<sup>-2</sup>, d) 0 mA cm<sup>-2</sup> (OCV). Gray values show the changes of normalized transmittances between 0.99 (black) and 1.01 (white). Irreversible fragment movements are observable, indicated by white arrows. The region shown is the same as in figure 4.**

For a better comparison of the transmittance changes in the fuel cell during operation at different conditions, profiles were calculated along horizontal lines through the radiographs in figures 5-7. The position of two of such lines is marked in Figure 5c and Figure 8a. The line plots have a width of 1 mm (i.e. all transmittance values have been averaged over 1 mm width) and were taken from the channel area over the whole width of the radiographs. Figure 8b-d show sets of line plots for cell HTT1 and HTT2. Each line plot corresponds to a given operating condition defined by the respective stoichiometry and current density.



**Figure 8:** a) Normalized radiograph taken at OCV condition and  $\lambda_{An/Ca} = 4/4$ . The plots were obtained by averaging transversal along the path represented by the black markers as the path was congruent with the lower channel. This was performed in Figure 5, Figure 6 and Figure 7. b) Cell HTT1 (with break-in procedure) for a stoichiometry of  $\lambda = 2/2$  and c)  $\lambda = 4/4$  and d) cell HTT2 (without break-in procedure). Pronounced peaks originate from displacement of fragments.

## 5 Discussion

Due to the different attenuation coefficients of ortho- and pyro-phosphoric acid the hydration by product water during the fuel cell reaction or the dehydration at OCV of the acid implies a significant change on the overall transmittance. However, the presented line plots show no significant change of the overall transmittance with respect to the reference state (OCV). This indicates that neither homogenous hydration nor dehydration of the phosphoric acid took place inside the MEA of the fuel cell within the observed area about  $7.3 \times 4.0 \text{ mm}^2$  during the measuring period of about 24 h.

To analyze the possible reasons for the local changes in transmittance observed during the measurements variations of material thickness and composition must be taken into account. Local transmittance changes can be caused by different effects:

1. Chemical changes e.g.  $\text{H}_3\text{PO}_4 \rightarrow \text{H}_4\text{P}_2\text{O}_7$  and vice versa
2. Filling of empty pores with  $\text{H}_3\text{PO}_4$ ,  $\text{H}_4\text{P}_2\text{O}_7$  or ABPBI

Table 1 summarizes the scenarios of material conversion and redistribution that could account for relative transmittance changes in the range of  $-0.8\% \leq \Delta T \leq 0.7\%$ . This interval was chosen with respect to the detected transmittance variations given in Figure 8. This includes hydration and dehydration of phosphoric acid, membrane swelling as well as subsequent warping of the membrane. The thicknesses were calculated using

$$d(T_{load}, \mu_1, \mu_2) = \ln \frac{T_{load}}{T_{OCV}} / (\mu_2 - \mu_1) \quad (1)$$

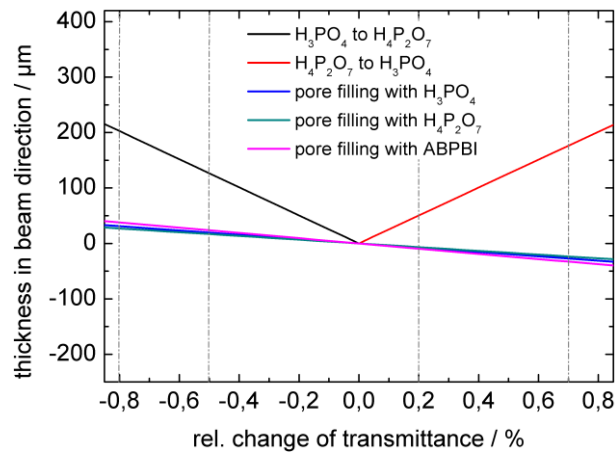
which is a variant of the Beer-Lambert's law under the simplifying assumption that all other conditions remain constant. Here,  $d(T_{load}, \mu_1, \mu_2)$  denotes the thickness of the transmitted layer in which the present material with attenuation coefficient  $\mu_1$  was "converted" into another material with attenuation coefficient  $\mu_2$ .  $T_{load}/T_{OCV}$  is the change of relative transmittance. Changes of material thickness can be induced by replacing, redistributing (adding or removing of material in the field of view, which lead to locally changed transmittances) or swelling. The calculation was performed for different assumed materials in the MEA. Table 1 includes coefficient differences between various phosphoric acid derivatives and membrane material as well as gaseous  $\text{H}_2$ ,  $\text{O}_2$ , steam or air in

“empty” pores inside the MEA components. The thickness  $d_{\Delta T=x}$  (x stands for a change of transmittance in percent) refers to the thickness of transmitted material that is affected by the assumed material changes in order to achieve a transmittance changes of  $\Delta T=x$ .

	$\mu_2-\mu_1 / \text{mm}^{-1}$	$d_{\Delta T=-0.8\%} / \mu\text{m}$	$d_{\Delta T=-0.5\%} / \mu\text{m}$	$d_{\Delta T=0.2\%} / \mu\text{m}$	$d_{\Delta T=0.7\%} / \mu\text{m}$
$\text{H}_3\text{PO}_4 \rightarrow \text{H}_4\text{P}_2\text{O}_7$	-0.0396	203	127	-	-
$\text{H}_4\text{P}_2\text{O}_7 \rightarrow \text{H}_3\text{PO}_4$	0.0396	-	-	50	176
pores $\rightarrow \text{H}_3\text{PO}_4$	0.2571	31	19	-8	-27
pores $\rightarrow \text{H}_4\text{P}_2\text{O}_7$	0.2967	27	17	-7	-24
pores $\rightarrow \text{ABPBI}$	0.2120	38	24	-9	-33

**Table 1: Attenuation coefficients and differences of attenuation coefficient between various phosphoric acid derivatives and membrane material. Thickness  $d_{\Delta T=x}$  (x stands for change of transmittance, rounded to integer  $\mu\text{m}$ ) refers to the thickness that is necessary to achieve changes in the transmittance by replacing acid volumes or filling pores in the MEA in beam direction and can be obtained using eq. (1). Negative values mean that initially filled pores are emptied. “-” means that the changes in transmittance cannot be caused by the corresponding effect (different algebraic signs).**

As an example we consider a relative transmittance change of -0.5 % which is a typical value measured for HTT1 at  $600 \text{ mA cm}^{-2}$ . If this change was exclusively generated by the substitution of  $\text{H}_3\text{PO}_4$  for  $\text{H}_4\text{P}_2\text{O}_7$  the corresponding thickness of the converted material layer would be  $127 \mu\text{m}$ . Taking into account the initial MEA thickness at OCV and the amount of phosphoric acid added into the MEA (as described in Sec. 3.2) this value appears unrealistically high. More likely, the chemical conversion of phosphoric acid is accompanied by a redistribution of the acid derivatives. While acid is pressed into other membrane regions pores are filled or depleted. This causes a warp and a tilt of the fragments which are attached to the membrane. Both, filling of pores and tilting of the membrane into the viewing direction, contribute to an increased projected material thickness and a higher attenuation (e.g. as calculated in lines 3-5 of Table 1 in case of pore filling). Figure 9 demonstrates the influence of a varying material thickness produced by membrane swelling and by the conversion of phosphoric acid. Since the beam attenuation by gaseous phases is negligible small ( $< 0.01\%$ ) the filling of empty pores with acid derivatives or membrane materials results in stronger changes of the transmittance as compared to the sole conversion of acid derivatives.



**Figure 9: Correlation of change in relative transmittance and material thickness in beam direction. Dotted lines mark the transmittances used for calculations in Table 1.**

With respect to the magnitude of measured changes it is reasonable to assume a combination of superposed material redistributions to be responsible for local transmittance variations. A clear distinction of the individual effects is, however, not possible, because measurements in through-plane perspective only yield an overall transmittance signal across MEA and GDLs.

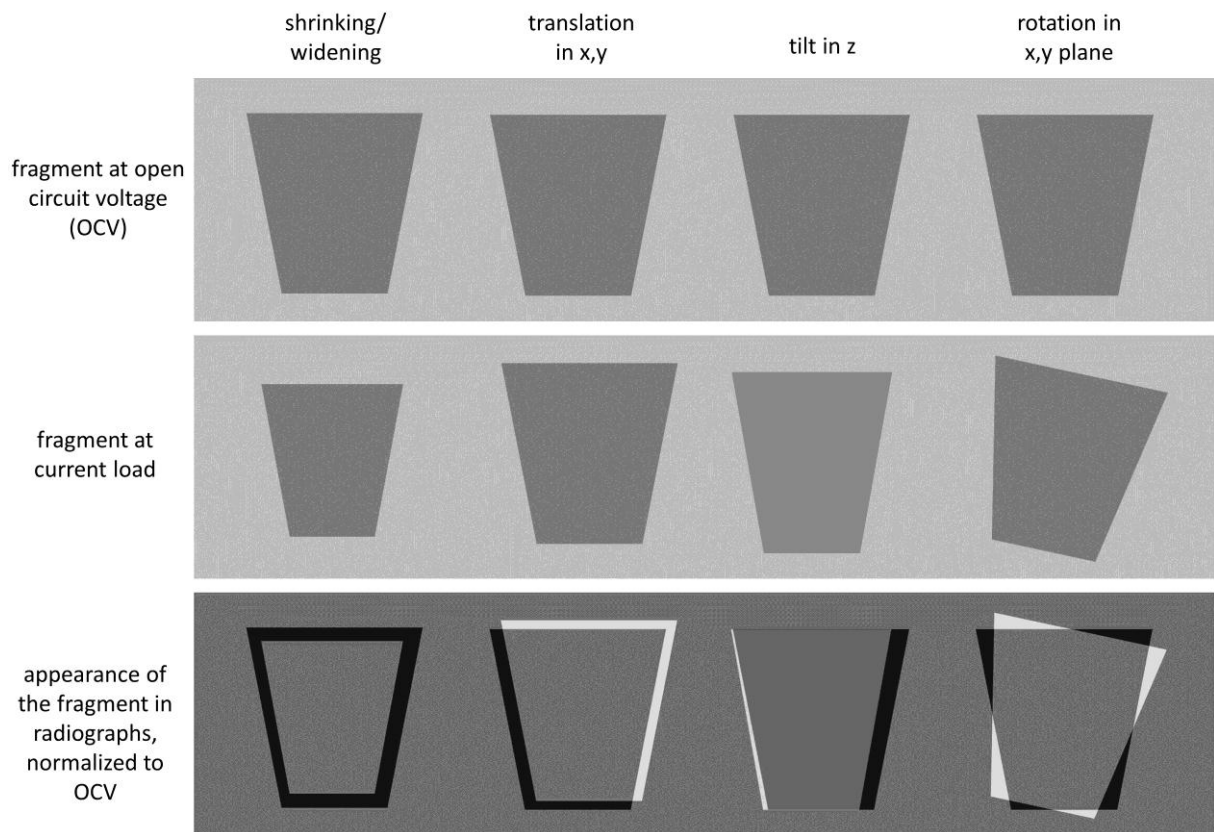
Images in figures 5 and 6 and the line plots presented in figure 8 show that changes of local transmittances are more pronounced in cell HTT1 which was subjected to a break-in procedure. In freshly assembled fuel cells the phosphoric acid spreads within the MEA components during the break-in procedure due to evolving product water. One possible explanation for the found periodical material redistributions can be the hygroscopic properties of the phosphoric acid. Up to now, there are no investigations on HT-PEFCs concerning the impact of water agglomerations (gaseous or fluid) on the distribution of phosphoric acid. Due to locally changing properties of the MEA such as membrane thickness, cell compression or fluctuating doping with phosphoric acid, we assume locally changing properties for HT-PEFCs, too, implying varying impact of the hygroscopic properties. Thus, gaseous water is influenced by phosphoric acid agglomerations. The hygroscopic nature of phosphoric acid causes water to move to acid-rich regions, resulting in a decreased viscosity of the acid [35]. At lower viscosity the acid molecules have a higher mobility which facilitates acid rearrangements and, therefore, a more pronounced inhomogeneity of local acid distribution. Theoretically, upon changing to OCV conditions no water is produced at the electrode. As a result, water slowly diffuses out of the membrane and acid concentration and local distribution equilibrates nearly back to the initial conditions. This explains the reversibility and local nature of this effect (figures 5-7). The authors assume that the phosphoric acid doping technique is responsible for

the fixed location of transmittance changes (i.e. the periodic structure). It is still not clear why the changes in media distribution in cell HTT1 is less pronounced.

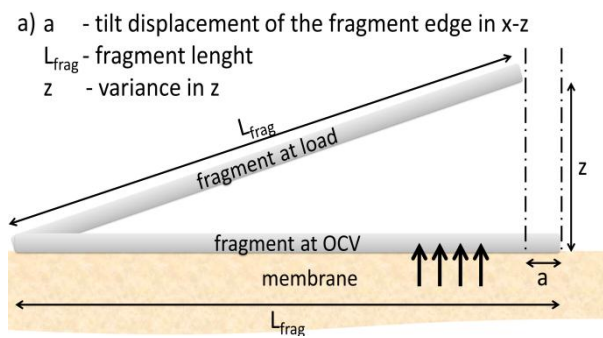
In the next part we will have a closer look on the variations of transmittance values at the edges of some electrode fragments (see Figure 6c and 6d and at the right top of Figure 7c and 7d), indicating displacement with respect to their initial position in the reference OCV condition. Since the respective fragments are all situated within areas of significant transmittance change, it is reasonable to assign fragment displacement to local deformation of the MEA. Especially for cell HTT2, some of the fragment displacements are obviously irreversible, see figure 7d. Therefore, material redistributions induced by load changes are assumed to modify the fragmented structure of the electrode permanently. Figure 10 illustrates different possible fragment movements and their corresponding appearance in the normalized radiographs. Also combinations of the effects are possible.

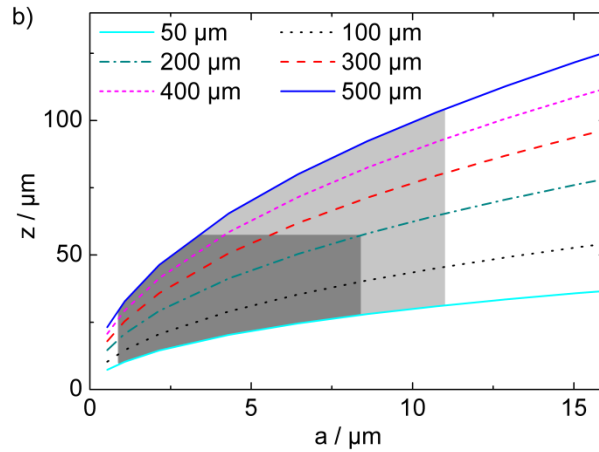
The found bright areas at the edges of the electrode fragments could not only be caused by shrinking/expanding or horizontal movement of the individual electrode fragments, but also by tilting of the fragments that is caused by a local swelling of the membrane (see Figure 10, third column). Figure 11a explains the relation between the fragment dimensions  $L_{frag}$  and the width  $a$  of the bright area at the edge of a fragment. Size of most fragments ranges from 50 to 500  $\mu\text{m}$  diameter. Figure 11b shows the dependence of fragment dimensions and the edge displacement  $a$  on the lift height of fragment edges  $z$  (see Figure 11a). The graphs were computed using the geometrical considerations given in eq. (2).

$$z = L_{fragment} \cdot \sin\left(\arccos\frac{L_{fragment} - a}{L_{fragment}}\right) \quad (2)$$



**Figure 10: Possibilities of fragment variances and the corresponding appearance in the normalized radiographs: shrinking/widening, translation, tilting or rotation.**





**Figure 11: a) Sketch of geometrical correlations for a tilted fragment. b) Correlation of tilt displacement  $a$  and lift (height)  $z$  of the fragment edge for typical fragment dimensions  $L_{frag} \approx 50-500 \mu\text{m}$ . The light gray areas mark actual combinations of fragment dimension  $L_{frag}$  and tilt displacement  $a$  as found in the radiographs. The dark gray area schematically highlights the most frequently occurring combinations.**

The gray areas in Figure 11b include all combinations of fragment dimensions and tilt displacements found in the normalized radiographs. Frequently measured combinations are highlighted in dark gray indicating that most variances of the fragment position in the  $z$ -direction are in the range of 20-60  $\mu\text{m}$ . The magnitude of these values are in line with the calculated changes of material thickness necessary to induce the observed variation of local transmittance and it also matches with the total thickness of the MEA which can be seen as a lower and upper physical limit for maximum fragment tilts here.

We interpret all of the found structural changes (the periodical structures and the electrode fragment movements) as a symptom or cause of MEA degradation but their impact on the total active catalyst surface is not yet clear. One cannot exclude that fragments detach or are destroyed by the forces occurring and, therewith, modify the electrical and transport properties of the electrodes [36].

## 6 Summary

We present the first synchrotron X-ray radiographic in-situ study on high-temperature polymer electrolyte fuel cells (HT-PEFCs) in the through-plane viewing direction. A cell that had been subjected to a break-in procedure and a freshly assembled one were analyzed at different flow rates and current densities. The analysis reveals new details about dynamic effects in HT-PEFCs, especially about the redistribution of phosphoric acid inside the membrane electrode assembly (MEA).



However, upon increasing current density changes in the local transmittance were observed in the MEA which are assumed to be caused by non-uniform doping of the electrodes with phosphoric acid. The typical widths of regions of altered transmittance were about 1 mm. Within channel areas local transmittance variations were more pronounced as compared to rib areas. The origin of transmittance changes was largely attributed to a redistribution of phosphoric acid inside the MEA. Due to the hygroscopic nature phosphoric acid attracts (product) water. While the phosphoric acid is diluted its viscosity decreases and the higher molecule mobility can facilitate local acid redistributions. The effect is more pronounced under the channels because of the lower local compression rate of the MEA which permits a stronger membrane deformation. Transmittance changes increase with increasing current densities and depend only slightly on the applied stoichiometry. All observed effects were less pronounced when no break-in procedure was applied to the cell.

The redistribution of phosphoric acid yields variations of the fragmented structure of the electrodes. The strength of the tilt of electrode fragments was found to be in accordance with the expansion and the contraction of the MEA. The comparison of radiographs taken during OCV condition before and after an operation sequence of increasing load conditions revealed irreversible modifications of the fragment structure of the catalyst layers.

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