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Influence of Artificial Ageing of Gas Diffusion Layers on the Water Management of PEM Fuel Cells

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Abstract

The influence of artificial ageing of gas diffusion layers (GDL) on the water management within the GDL was investigated in-situ by synchrotron X-ray radiography. One GDL was subjected to an accelerated ageing procedure in 30 % H_2O_2 solution while another GDL was pristine. The GDLs were first assembled in test cells, after which the water distribution during operation was investigated. Radiographic measurements were combined with temporally resolved electrical analyses. Significant differences in cell voltage and water accumulation were observed in the GDL operated at steady-state conditions. In the cell containing the aged GDL, a higher water volume was found especially at the anode side while the cell voltage was lower.

Introduction

Up to now, the ageing mechanisms in gas diffusion layers (GDL) of polymer electrolyte membrane (PEM) fuel cells are still not completely understood. Successful long-term tests have been completed by different research groups and interested parties [1]. Besides high manufacturing costs, the long-term stability of the cells still remains a problem. Several thousand hours of reliable operation are required for stationary or mobile applications. Various artificial ageing experiments have been performed to overcome the problem of insufficient cell durability [2,3,4,5,6].

One approach to artificial ageing is to insert GDLs into hot hydrogen peroxide (H_2O_2) solution [7]. The chemical reaction corrodes the GDL material. As a result, the contact angle between water and GDL surface is reduced indicating decreased hydrophobicity of the GDL. This has a severe impact on water management due to the significant change to the capability of water transport.

Synchrotron X-ray imaging is a non-destructive method that can provide insights into operating fuel cells at high spatial and temporal resolution and has been widely used in the past [8,9,10,11,12,13,14,15,16,17,18,19,20,21,22].

In this work, we applied an artificial ageing procedure to a Freudenberg H2315 GDL (containing a microporous layer, in short "MPL") and investigated the effect of this procedure on cell performance and water distribution [23].

Setup

Accelerated ageing

Ageing of the GDL material - including its microporous layer but not the membrane - was done by accelerated ageing [24]. This artificial ageing method is related to the chemical environment inside an operating cell which can occur at high cell voltages [25,26]. Beside water, hydrogen peroxide can be produced during certain operating conditions (preferentially at high cell voltages, i.e. above 0.6 V). Pictures of the accelerated ageing setup are shown in Figure 1.

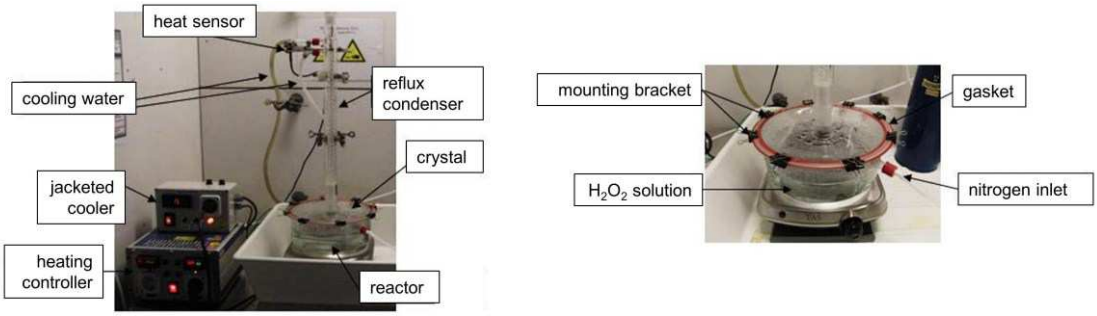

Figure 1. Reactor for accelerated ageing of gas diffusion layers in liquid H_2O_2. Right figure shows the whole aperture while left figure shows a close-up of the reactor chamber.

One GDL was put into a 30 % solution of hydrogen peroxide (diluted with water) at 90°C for 24 h. During this ageing process, especially the carbon fibers of the GDL will be corroded by H_2O_2. Consequently, the surface properties of the fibers change, in particular their hydrophobicity. The aged GDL was assembled to a fuel cell ("test cell 2") on both the anode and cathode sides. Another GDL of the same type and production batch as the first was not subjected to hydrogen peroxide. This GDL was assembled to "test cell 1" again on both sides.

Radiography setup

Radiographic measurements were done at the tomography station BAMline at the Helmholtz-Zentrum Berlin (electron storage ring BESSY 2) [27,28]. An optical setup (Figure 2a) with a pixel resolution of 2.1 µm was chosen to obtain sufficient spatial resolution - on the one hand - and a temporal resolution of 5 s with good measurement statistics for water quantification - on the other. The energy of the synchrotron beam was adjusted to 17 keV.

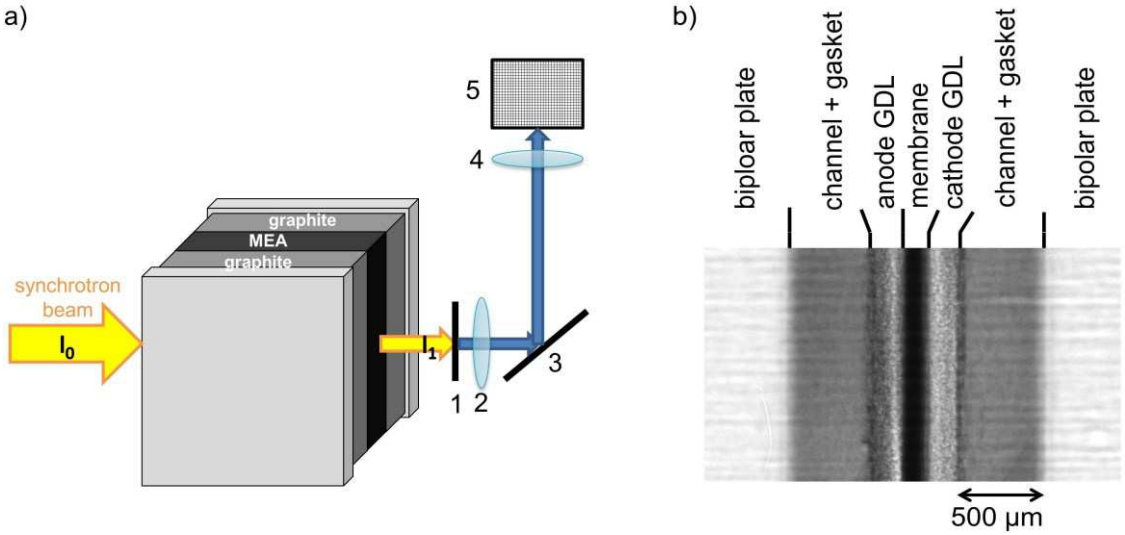

Figure 2. a) Sketch of the radiography setup. 1 – scintillator, 2 – objective, 3 – mirror, 4 – microscope, 5 – CCD chip. b) Radiograph of a cell which was irradiated in the in-plane direction. All cell components are shown side by side.

Imaging and electric measurements were carried out simultaneously. Two test cells were analyzed. Test cell 1 contained the fresh and test cell 2 the aged GDL [29,30]. Each operation point was held for around 30 min to achieve steady state conditions at the end of the holding time. Two different reactant gas humidities (50 % r.h. and 100 % r.h.) were used at a constant current density of 1.5 A/cm^2. Using this setting, several hundreds of radiographs were obtained for each operating point. Figure 2b shows an exemplary radiograph (radiation in the in-plane direction). Using such images, the impact of aged GDLs placed at the anode and cathode sides on the water distribution can be visualized.

A fuel cell design adapted to the conditions during synchrotron radiography was used. Cooling, compression and channel design were identical to state-of-the-art fuel cells, whereas the active region of the test cells was reduced to about 3.9 cm^2. The reduction was done to limit the area of water characterization to the area of water production within the active area without any effect on water transport from regions out of sight. The membrane electrode assembly was a GORE PRIMEA 5761.

Results

The surface contact angles were measured on both sides of each GDL at the MPL and at the substrate side (see Table 1). The measurements took place before assembly of the fuel cells and the start of radiographic measurements. The ageing procedure clearly reduced the contact angle of the GDL by up to about 14 %.

Table 1. Contact angles of fresh (test cell 1) and aged (test cell 2) GDL at MPL and substrate side.

	Contact angle at MPL side / °	Contact angle at substrate side / °
Test cell 1	165.4 ± 0.23	148.9 ± 0.34
Test cell 2	142.4 ± 0.23	136.8 ± 0.23

We calculated the thicknesses of the evolving water layer which is transmitted by the beam for both operating points of the test cells. Three radiographs of the measurement of test cell 2 are shown in Figure 3.

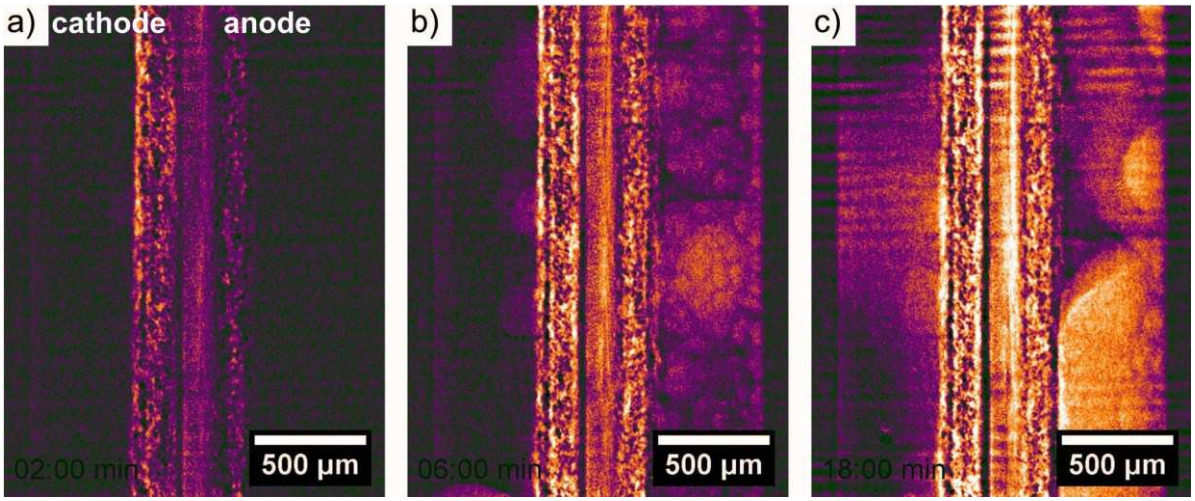

Figure 3. Water evolution in a test cell 2 operated at 1.5 A/cm^2 and 50 % relative humidity after a) 2 min, b) 6 min and c) 18 min.

The results of the quantitative analysis of the radiographic measurements are shown in Figure 4. This figure shows the temporal evolution of water in the substrate of the gas diffusion layers at the anode and cathode sides for different humidities of the reactant gases as a difference to the water content at open circuit voltage (OCV) at t = 0 s. The first operating point (shown in red color) has been performed without drawing current in order to humidify the membrane and resulting in membrane swelling. Membrane swelling causes a movement of other fuel cell components, e.g. displacement of single GDL fibers. This membrane movement is later corrected by image analysis in order to reduce imaging artefacts during quantification of the water distribution.

Further operating points were started at constant current density (j = 1.5 A/cm^2), cell temperature (T_{cell} = 50°C) and pressure (1 bar). The higher gas flow rate simulates operating at the usually used stoichiometry. The active area was 3.9 cm², which prevented blockage of channels or GDL pores due to insufficient condensate removal. Only the humidity of the reactant gases was varied between 50 % and 100 % relative humidity.

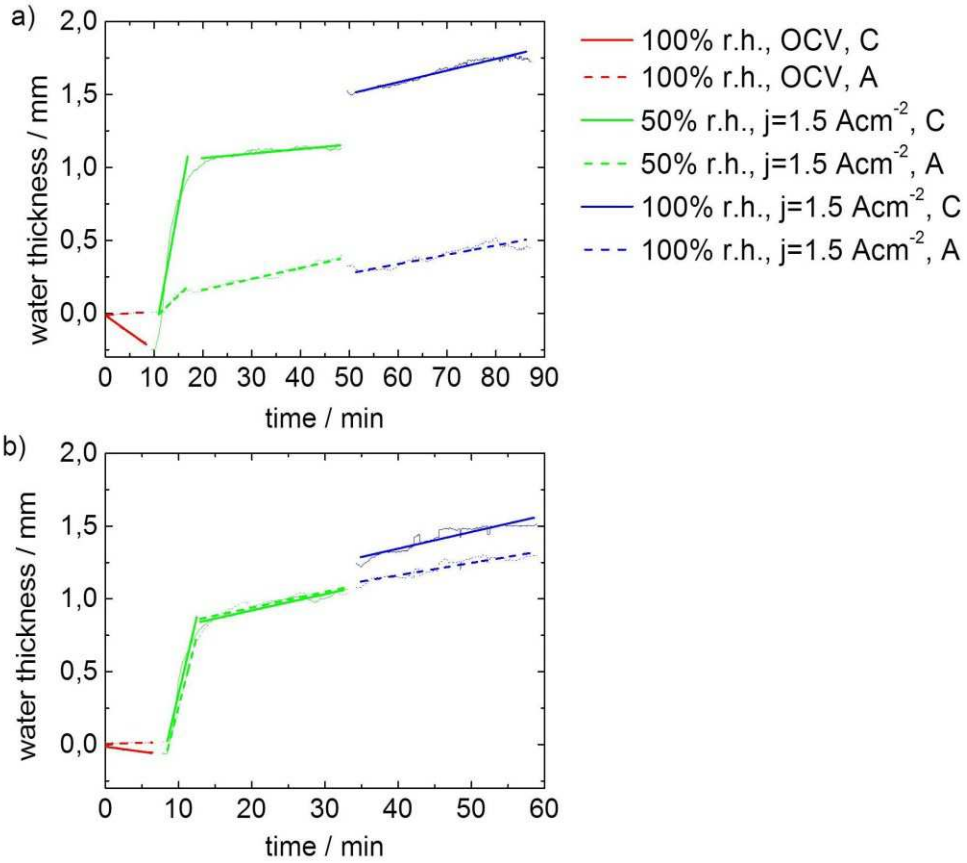

Figure 4. Water accumulation in a GDL at different operating conditions in dependence of accelerated ageing. "A" – anode, "C" – cathode. a) Fresh GDL, b) aged GDL. Trend lines are also given. Red lines: 0 A/cm^2, 100 % r.h.; green lines: j = 1.5 A/cm^2, 50 % r.h.; blue lines: 1.5 A/cm^2, 100 % r.h.; dotted lines: anode.

Table 2 gives the averaged water thicknesses in the GDLs for the last 10 min of each operating point. This ensures measurements of water thickness at steady state conditions. Channel water was not considered although it can influence the measured water accumulations in the GDL. A comparison between aged and the fresh GDLs reveals a significant increase of water thickness at anode for the aged GDL.

Table 2. Average water thickness at steady state conditions for 50 % r. h. and 100 % r. h.. "A" – anode, "C" – cathode. Calculation based on data from Figure 4.

	water thickness at 50 % r.h. / mm	water thickness at 100 % r.h. / mm
test cell 1	C: 1.13 / A: 0.34	C: 1.75 / A: 0.47
test cell 2	C: 1.01 / A: 1.02	C: 1.49 / A: 1.28

Table 3 presents cell voltages averaged over the last 10 min. of each operating point. Like the water thicknesses, the voltages of the test cells differ; test cell 1 with the fresh GDL delivered a higher voltage than test cell 2 which contained the aged GDL. The voltages of both cells are slightly increased at higher gas humidity.

Table 3. Cell voltages of test cell 1 and test cell 2 for different gas humidities (simultaneously measured during radiography).

	cell voltage at 50 % r.h. / mV	cell voltage at 100 % r.h. / mV
test cell 1	427	434
test cell 2	291	308

Discussion

A decrease of contact angles is mostly attributed to a decrease of PTFE content of the GDL material. Our measurements have shown a decrease of the contact angle of about 13.9 % on the MPL side and of 8.1 % on the substrate side.

While the water thickness on the cathode side remained unchanged after GDL ageing, an increase on the anode side is obvious. This can block gas transport paths through the GDL material. Blocked paths hamper the transport of reactant gases between channels and GDL and therefore have a notable impact on cell performance. After ageing, the cell voltage decreased by about 30 %, whereby the decrease is less pronounced for operation points at high reactant gas humidities. The lowered contact angles obviously lead to water agglomerations and subsequently to hindered gas transport in the anode GDL [31,32]. Here, water accumulations in the anode GDL lead to a reduction of cell performance.

A still open question is how our artificial ageing procedure is related to real ageing of GDLs in fuel cells. In the literature, two different views can be found. Zhang et al. [33] reported that the cathode was the main point of hydrogen peroxide attack. In contrast, Liu and Zuckerbrod presented data indicating that hydrogen peroxide was generated mainly at the anode [34]. We have aged both sides with hydrogen peroxide, but only anode aging does have a significant impact on the overall fuel cell performance.

Summary

Two Freudenberg H2315 series gas diffusion layers (GDL) taken from the same production batch were used in identically designed fuel cells. One GDL was fresh, i.e. not intentionally aged, the other one was subjected to an artificial, accelerated ageing procedure for 24 h in a 30 % hydrogen peroxide solution. In-situ synchrotron radiography and electrical measurements were performed using test cells and were supplemented by ex-situ contact angle investigations.

As one result, a significant increase of water thickness at the anode side was found for the aged GDL for 50 % relative humidity (r.h.) and for 100 % r.h. The strongest changes in water thickness were observable in the first few minutes after switching from OCV to current conditions for both GDLs. In contrast to the cell containing the fresh GDL, the cell containing the aged GDL showed a decrease of cell voltage. It is assumed, that blocked gas paths inside the anode GDL decrease the performance of the fuel cell due to fuel starvation.

Acknowledgements

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