Energy 102 (2016) 161–165

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Investigation of water transport dynamics in polymer electrolyte membrane fuel cells based on high porous micro porous layers

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ARTICLE INFO

Article history:
Received 13 December 2015
Received in revised form
30 January 2016
Accepted 12 February 2016
Available online xxx

Keywords:
Polymer electrolyte membrane fuel cell
Microporous layer
Water transport
Radiography
Tomography
Synchrotron X-ray imaging

ABSTRACT

In this study, synchrotron X-ray imaging is used to investigate the water transport inside newly developed GDM (gas diffusion medium) in polymer electrolyte membrane fuel cells. Two different measurement techniques, namely in-situ radiography and quasi-in-situ tomography were combined to reveal the relationship between the structure of the MPL (microporous layer), the operation temperature and the water flow. The newly developed MPL is equipped with randomly arranged holes. It was found that these holes strongly influence the overall water transport in the whole adjacent GDM. The holes act as nuclei for water transport paths through the GDM. In the future, such tailored GDMs could be used to optimize the efficiency and operating conditions of polymer electrolyte membrane fuel cells.

1. Introduction

Fuel cells combined with electric motors are expected to offer alternatives to conventional engines powered by fossil fuels in both mobile and stationary applications [1,2]. For transportation, and here especially in the automotive sector, PEMFC (polymer electrolyte membrane fuel cells) are considered the most promising fuel cell type.

In such PEMFC, a careful water management is crucial to prevent two unfavorable operation situations: Excessive drying of the membrane and flooding of the diffusion media, which was found for example by Wang et al. [1,3–5]. In the first case, the membrane shrinks and loses its proton conductivity, which decreases fuel cell efficiency. In the second case, liquid water in the cell materials blocks gas flow to the catalyst layers. As a consequence, the catalyst layers are undersupplied with gas and the cell performance drops. Hence, a well-balanced water management is an essential condition for optimum power output and long term stability.

Optimization of the water transport in the gas diffusion and the microporous layers leads to a better efficiency especially under critical operation conditions that promote flooding. Such conditions include temperatures below 60 °C as well as high currents that both give rise to elevated water contents [6–9]. There are many possible ways to design the GDM (gas diffusion medium), which consists of the GDL (gas diffusion layer) and, in most cases, a MPL (microporous layer). The morphology and the composition of the fiber substrate (namely the GDL) and the microporous material strongly influence water accumulation and transport [1,10–13]. Different modeling approaches were used to analyze and optimize mass transfer within the porous materials [14–29].

Because neutrons are strongly scattered by hydrogen, imaging methods based on neutrons are very useful to investigated hydrogen distributions within a material [30–35]. For the same reason, neutron imaging is frequently used to investigate the water distribution in operating fuel cells [36–53]. Synchrotron and lab-based X-ray radiography and tomography have been used for investigation of water/media distribution with much higher spatial

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http://dx.doi.org/10.1016/j.energy.2016.02.075
0360-5442/

resolutions of a few μm, what is enough to resolve the water distribution inside the GDL pores and MPL/electrode in sufficient detail [54–69]. Recently, a more detailed understanding of the influence of GDM morphology was obtained by analyzing treated GDM materials and punching holes into the fiber substrate [70–72]. It was shown, that such GDM can significantly improve the performance of a cell [73,74].

In this study, a modified Freudenberg MPL material with randomly arranged holes is subjected to synchrotron X-ray imaging to investigate the dynamic liquid water transport behavior. The modified material is compared to unmodified reference material at two different cell temperatures.

2. Experiments

The experiments were carried out using two PEMFC with active areas of 5.4 cm^2 and flow fields that contain seven parallel vertical channels. The first cell contains a modified MEA (membrane electrode assembly), which consists of a CCM (catalyst-coated membrane) equipped with a GDL (gas diffusion layer) from Freudenberg based on a H1411 fiber substrate, while the second cell contains a reference MEA consisting of a CCM equipped with a H1410 I4 C10 GDL. The modified GDM has an uncompressed thickness of 201 μm and includes a newly developed MPL with arbitrarily distributed holes with diameters ranging up to 30 μm. During the experiment, fuel cell operation was held at a current density of 1 A/cm^2 at stoichiometric ratios of 5 at both the cathode and anode sides. Cell temperatures of 40 °C and 55 °C were used and compared in this study.

The cell is investigated with synchrotron X-ray radiography and tomography of a region centered in the middle of the vertical cell extension and in an area covering ~10% of the total active area as used by Alink et al. [70].

The measurements were performed at the imaging beamline "BAMline" at the synchrotron electron storage ring Bessy II in Berlin, Germany which is described by Görner et al. [75]. The detector contained 4008 × 2672 pixels, each 2.2 μm × 2.2 μm wide, which corresponds to the observed field of view of 8.8 mm × 5.9 mm. During radiography, images were acquired with an exposure time of 2 s. Tomographies were acquired with 3600 projection images over an angular range of 360° within a total acquisition time of about 2.5 h. A photon energy of 19 keV was selected by a W/Si double multilayer monochromator with an energy resolution ΔE/E~1.5%, ensuring sufficient transmission through the cell materials.

The beam transmission was calculated via image processing with flat field images containing the plain beam without the cell and dark field images without beam. First the cell was tomographed in the dry condition. Then, during operation, the cell was radiographed to capture the transport dynamics of the evolving liquid product water in the cell components. After the dynamic radiographic experiments, cell operation was stopped and the cell was tomographed in order to capture the water distribution inside the fuel cell components. This technique allows for a detailed analysis of the transport dynamics, which are captured in the radiographic projection data of the three-dimensional structure of the cell materials as well as the 3D resolved water distribution during operation at a given time by Krüger et al. [76].

3. Results

At 40 °C, the voltage for the reference cell was 500 mV, whereas the cell with the modified material achieved 550 mV with otherwise identical operation parameters. Krüger et al. Markötter et al. and Sasabe et al. found that cracks in the MPL are seed points (nuclei) of liquid water transport paths through the GDL [76–78]. In the present case, the large MPL pores might play a similar role as the cracks: They facilitate accumulation of liquid water. The emerging product water then moves from the holes through the GDL into the channel, from where droplets are removed continuously by the gas stream. In some cases, the water is always transported through the same passage, which leads to droplets originating at the very same positions over and over again.

The tomographic image data of the dry and operated state has been matched in order to extract the water distribution. Fig. 1 shows a cross section for the fuel cell (A), a cut slice in the dry state (B), the operated state (C) and the extracted water distribution (D). The slice is oriented parallel to the cell material positioned in the cathode MPL. The dry state exhibits the holes in the MPL and due to the non-uniform structure also some intruding carbon fibers. In the operated state, we find some of those holes filled with liquid water. The attenuation coefficient alone does not allow one to distinguish water and MPL material in a reliable way. However, the difference between these two states provides the water distribution as pointed out by the arrows in Fig. 1(D). The tomographic data indicates that about 70% of the holes in the optimized GDM are filled with liquid water.

From the radiographic data we see that only a very few paths are used for water transport. In Fig. 2(A) we can see a water activity map and in Fig. 2(B) the water distribution of a cutout (3 mm × 1 mm) of the complete field of view, which includes three marked droplets as very active points that are building up again and again. The activity map highlights areas with strong temporal fluctuations of beam attenuation, which especially applies to the droplets. The temporal activity $A_t(x,y)$ at a given pixel position (x,y) is defined as

$$A_t = \frac{1}{t^*N}\sum_{k=2}^{N} | d_k(x,y) - d_{k-1}(x,y)|,$$

where N is the total number of images, d the local water depth and t the exposure time of each image. For pixels that do not change their grey value, $A_t = 0$ (black in Fig. 2). Pixels that fluctuate in intensity (water depth) have non-zero values (colors in Fig. 2).

Fig. 2(D) displays the water volume as a function of time for a region containing one of the droplets, see Fig. 2(C), which shows a radiographic still of droplet #3. As becomes visible in the graph, a droplet first builds up and is then carried away after some time by the gas stream. This happens periodically roughly every 30 s and results in a significant decrease of the measured water volume. The droplet grows at a rate of 0.13 nl/s, as derived from the slopes of the graph in Fig. 2(D). For droplets #1 and #2 shown in Fig. 2(B), the corresponding volume increase rate was 0.22 nl/s and 0.37 nl/s, respectively. These growth rates are related to electrochemically active areas of 0.23, 0.40 and 0.14 mm^2 for droplets 1, 2 and 3, respectively. Therefore, the corresponding transport paths through the GDL make an important contribution to the overall liquid water transfer through the GDL. Note that in the projection direction the complete water volume is analyzed, which includes the channels and, therefore, is subject to small variations due to water droplets passing the channel from time to time. This can be seen at the offset and short peaks in the graph (for example at 280 s).

Fig. 3 displays water activity maps for the modified and for the reference materials at two operation temperatures, 40 °C in Fig. 3(A) and (C) and 55 °C in Fig. 3(B) and (D), respectively. The four cathodic flow field channels in the mapped area can be seen clearly because they transport large amounts of water. Bright areas (Fig. 3(A), circles) indicate the presence of well-defined fast water transport paths. In Fig. 3(B–D) no such paths were found.