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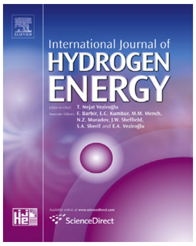

Evaluation of structural changes of HT-PEFC electrodes from in-situ synchrotron X-ray radiographs

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ABSTRACT

One of the main goals for improvement of high-temperature polymer electrolyte fuel cells (HT-PEFCs) is the increase of the fuel cell performance under different operating conditions. We investigated the correlation between operating conditions and structural changes in the electrodes by means of in-situ through-plane synchrotron X-ray radiography. From the radiographs it is possible to clearly distinguish between the electrode crack structure beneath the ribs and beneath the channels of the flow field. We present a statistical method to analyze these crack structures. For this purpose a ‘radar’ method was developed in order to obtain the width of the cracks at many different locations and the distribution of crack widths. We found a different behavior of cracks located beneath the ribs and beneath the channels and an influence of the operating conditions on local regions of the crack structure.

Introduction

High temperature polymer electrolyte fuel cells (HT-PEFCs) are typically operated at temperatures between 160 and 180 °C. Like classical PEFCs they are based on polymer electrolyte membranes. For the manufacturing of membrane electrode assemblies (MEA) several methods can be applied. Common to all of them is the production of a catalyst paste. The latter is applied either directly onto the membrane or onto the gas diffusion layer (GDL) by means of several coating techniques. The drying process leads to a characteristic structure of cracks in the membrane electrode assembly (MEA) as shown in Fig. 1 [1,2]. The morphology of the crack structure depends on the thickness of the electrode, the temperature and duration of the drying process, and the humidity in the laboratory. Not only the electrochemical active area is reduced by the cracks, in particular they affect the

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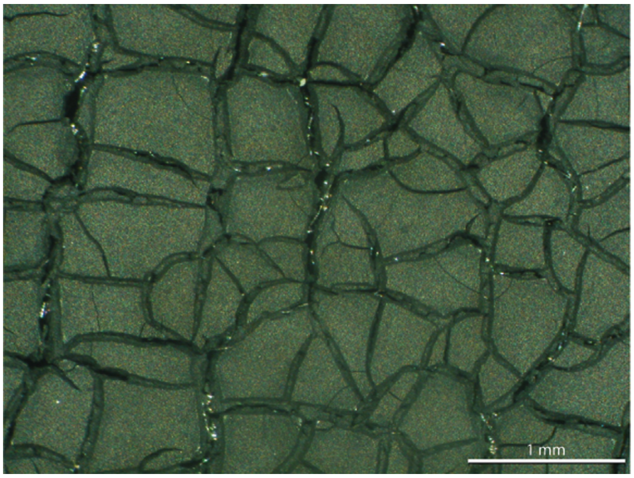

Fig. 1 – Optical microscopy image of cracks and blocks visible in the catalyst layer of a gas diffusion electrode of a direct methanol fuel cell (DMFC). The catalyst paste was applied to a decal substrate using a doctor blade. The crack structure depends on the manufacturing technique of the paste and the dispersion technique [1].

water transport in PEFCs [3–5]. Hence, an impact of the cracks on cell performance cannot be neglected.

Cracks in the manufactured electrodes can be easily characterized before stack assembly using several image processing techniques, e.g. scanning electron microscopy (SEM), transmission electron microscopy (TEM), light microscopy (see Fig. 1) but these techniques don't contain information regarding changing properties of the cracks and their impact on the cell performance under dynamic operation of the fuel cells.

Manke et al. [6], Sasabe et al. [7], Deevanhxay et al. [8], Markötter et al. [5], and Eller et al. [9] applied in-situ X-ray radiography on PEFCs to investigate water distribution in gas diffusion layers and micro-porous layers of PEFCs under varying operating conditions.

Regarding the manufacturing of PEFC MEAs, Wannek et al. [1] observed a relationship between the morphology of the cracks and the dispersing technology of applying the catalyst material on the decal substrate. They evaluated the amount of cracks in the dry catalyst layer related to the total area. Hizir et al. [10] used the same method to define the crack density in the micro porous layer (MPL) and the catalyst layer (CL). For characterizing the morphology of the surface they took a set of profiles obtained with optical profilometry. With this method they got a set of height profiles parallel to the coordinate axes and they evaluated six amplitude parameters defined by the British Standards [11].

Sasabe et al. [7], and Deevanhxay et al. [8] studied cracks in MPLs and GDLs which are another components in PEFCs. They used soft X-ray radiography for their studies. The breakthrough of water from the electrode into the GDL and its flow paths in MPL and GDL were analyzed.

Kundu et al. [4] classified the physical processes leading to degradation of fuel cells in presence of cracks. They identified cracking in the catalyst layer as one – but not the only one – defect in the manufacturing process of MEAs affecting the quality. As a consequence, comprehensive investigations are required not only on experimental studies but also on modeling the physical processes taking place in the wide area of degradation of the catalyst layer.

Pfrang et al. [12] observed cracks in the cathode CL via X-ray radiography. After marking the cracks manually in their images they investigated the 3D characteristic of the cracks regarding their volume in the CL. The crack density was also monitored.

Investigations on the design of CL often address the three-dimensional structure [13] or its effective parameters [14]. Cracks in the CL affect the interface between the CL and the MPL/GDL.

Arlt et al. [15] investigated the Pt and Ru concentration in the catalyst layers of a direct methanol fuel cell (DMFC) using synchrotron X-ray absorption edge imaging (NEXAFS/XANES). They found differences between areas located under the land and areas located under the ribs of the bipolar plate. Because Pt is located on both CL at the anode and cathode side, cracks in both CLs were observed as overlaid structure in the Pt images. On the other hand, only the cracks on the cathode side were found in the Ru images.

The fraction of cracks related to the whole area can easily be obtained by just counting the pixels after converting the image to black/white (BW) [1]. Other investigations are targeting the pore structure of the catalyst in nano scales. However, it is desirable to have an analytical method to quantify the morphology (or structure) of the cracks in the micro structure as it is visible in Fig. 1.

The importance of crack structures is well-known in various fields. Novák et al. [16] investigated cracked clay soil. There are numerous methods describing the movement of water transport in cracked soil [16]. Basically they can be separated into few classes of methods. The results of transport models based on crack networks often do not meet the requirements in the field of water transport in cracked soil [16]. The benefit of models which are using statistical properties of cracks (e.g., depths and widths) is that they do not require detailed knowledge of the crack system. Novák et al. [16] developed a detailed mathematical model to describe the water transport in the particular kind of cracks in swelling soil. Their method belongs to another class of methods featuring detailed physical modeling. Landry and Karpyn [17] investigated in fluid flow in fractured permeable media. For this purpose, they investigated cylindrical polyethylene rods with 0.127 cm in diameter. Their porous structure was obtained via X-ray radiography. Landry and Karpyn investigated in the cracks as means of fluid transport.

In contrast to the three-dimensional methods for crack analysis mentioned above we developed a novel method for quantitative analysis of the two-dimensional structures which can be observed already with light microscope or SEM images.

The optical setup to capture the images from the BESSY synchrotron limits their size. Details are discussed in Section 2.2. Therefore only a small number of blocks can be found in a single image – an example is shown in Fig. 2. With this restriction one has to be careful in evaluating the block related measures because their number might be too small for