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Identification of liquid water constraints in micro polymer electrolyte fuel cells without gas diffusion layers

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ABSTRACT

A simplified, miniaturized polymer electrolyte fuel cell without gas diffusion layers was investigated under operation by neutron radiography. By visualizing liquid water, it was possible to identify limiting effects, which are directly related to the simplified construction principle. Depending on the operation conditions, undesired water accumulation either in particular micro-channels or on the cathode catalyst layer as well as drying of the anode catalyst layer was observed. As a consequence, the design of a fuel cell without gas diffusion layers must take into account these limitations visualized by neutron radiography.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are suggested to power devices of different scales, ranging from pacemakers to vehicles. One advantage of PEFCs is the high efficiency due to direct conversion of chemical energy, stored in hydrogen, to electrical energy. In comparison to batteries, high energy densities are predicted for fuel cell systems including hydrogen storage [1], a fact which is of interest for portable electronic devices.

Simple down-scaling of fuel cell assemblies, originally developed for automotive application, is one way to obtain a miniaturized fuel cell [2–5]. Precise assembly and negative scaling effects create challenges that could hamper industrial production. One solution might be membrane-based designs, where micro-patterned parts are fixed onto the membrane [6–8]. Taking into account the proposed production processes, where the fuel cell stack is assembled in foil-type planar shape, designs without gas diffusion layer [9,10] become even more interesting due to easier assembly, easier tightening, and reduced number of parts.

Only few of the presented micro polymer electrolyte fuel cell concepts are able to deliver current densities at which mass transport limitations in technical fuel cells can occur [11]. However, the influence of liquid water is already crucial at lower current densities. Beneficial effects are remarkable, such as improved proton conductivity in the membrane [12] as well as the formation of triple-phase boundaries in the catalyst layer, which are needed for the hydrogen oxidation and the oxygen reduction reactions, respectively. Due to water being removed from the anode by the electrochemical drag [13], gases have to be humidified prior to being fed into the fuel cell.

Contradicting this statement, Nguyen and Chan [11] point out that space constraints in micro fuel cell systems end up in designs without an active water management; i.e. developers forego an external humidification and expect the anode to be humidified by diffusion of product water from the cathode. Metz et al. [14] realized a passive water management for a micro fuel cell by using capillary micro-structures. They only report about positive effects on the cathode side when the operation conditions are changed and drying can be avoided.

However, liquid water can reduce the access of hydrogen and oxidant to the catalyst sites, especially when the fuel cell is not optimized for liquid water removal. Although the Peclet number, which is typically low for miniaturized PEFCs, may be an indication for insufficiencies in water removal [11]. This effect might be detrimental in self-breathing concepts, as for example suggested by Xia and Chan [15] or Modroukas et al. [16], which rely on free convection for oxygen supply and water removal on the cathode side. Modeling predicts an increased power density for decreasing channel dimensions down to 5 μm because the effective area of the

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electrode is increased for comparable membrane size and reactant flows [2,17]. Experimental validation of such results is challenging due to pressure drop and water accumulation [1]. Otherwise, Cha et al. [18] could show that, in the case of a miniaturized fuel cell including a gas diffusion layer, small channels can have a positive influence on the performance.

Up to now many concepts for micro PEFC have been published, but a profound understanding about limiting effects under operation has to be further developed. The method of choice to visualize liquid water in a PEFC under operation is neutron radiography [19]. The concentration of gaseous water is too low to be visible in neutron radiograms. Based on the improved resolution of a new detector system [20], even *in-plane* radiography can be carried out, i.e. in parallel direction to the membrane plane [21]. Hence we can fulfill the demand of Nguyen and Chan [11] and apply a method to visualize liquid water in a miniaturized polymer electrolyte fuel cell while operating. The employed miniaturized PEFC was developed at Paul Scherrer Institut (PSI) and it proved its ability to deliver power densities in a similar order of magnitude as reported for technical polymer electrolyte fuel cells with several square centimeters of active area [22]. The cell is operated without gas diffusion layers (GDL). The advantages of this concept are easier assembly, smaller number of parts and easier sealing due to no porous parts being employed in the fuel cell. However, the functions of a GDL, such as fine gas distribution and electrical connection of the active sites, have to be fulfilled by the micro-channels and the catalyst layer.

2. Experimental

The micro PEFC was assembled by sandwiching a catalyst-coated membrane (CCM) between two micro flow fields. CCMs including three different membranes were employed: Nafion 112, Nafion 211, and Gore Primea 5710. Each CCM contained platinum loadings of 0.4 mg/cm^2 (cathode) and 0.1–0.15 mg/cm^2 (anode).

The micro-patterning of glassy carbon has been published elsewhere [23–26]. The three-step process offers a great flexibility to produce various flow field geometries. For these experiments, a meander consisting of seven parallel channels (type A) was applied as well as a meander with merging channels (type B), whose number is reduced along the flow field from eleven to three channels.

The trapezoid-shaped channels were 110 μm deep and 100 (top) to 60 μm (bottom) wide, with a channel-to-rib-ratio of 5/3. The flow fields were surrounded by gold-coated aluminum end plates, in which the functions of electrical contact, gas supply to the microstructures, temperature control, and mechanical compaction are combined. The pressure in contact areas was adjusted by four bolts to a value of 2.2 MPa.

Table 1
Detector pixel size and effective spatial resolution of the applied neutron radiography setups.

	Pixel size/μm	Effective spatial resolution / μm
Through-plane	2.3	13.5
In-plane	20	200

The fuel cell, situated in the neutron beam, was operated by a home-build fuel cell test bench, which permanently controls and monitors gas flows, gas humidification, pressure, temperature, current, and voltage. AC impedance at 1 kHz of the fuel cell was monitored by a Tsuruga 3566 measurement device in order to identify increases of the high frequency resistance caused by drying effects in the membrane.

The neutron radiography experiments were carried out at the ICON [27] beamline at the neutron spallation source SINQ [28] of PSI. For our investigations, *through-plane* as well as *in-plane* neutron radiography were utilized, i.e. perpendicular and parallel to the membrane plane (Fig. 1).

Different imaging setups were used for in-plane and through-plane imaging. For in-plane imaging, a setup with anisotropic resolution [21] was used, due to different resolution requirements according to the direction (the highest resolution is required in the direction across the membrane). The detector pixel sizes as well as the effective spatial resolution of both setups are listed in Table 1. The effective resolution is defined as the Full Width at Half Maximum (FWHM) of the Line Spread Function (LSF) of the imaging setup.

Radiograms were referenced with a radiogram recorded at open circuit voltage (OCV) under dry conditions [19]. Additionally, selected results were referenced with radiograms recorded under D_2/D_2O operation of the fuel cell to exclude misinterpretation possibly caused by membrane swelling. In a referenced *in-plane* radiogram, the water content was obtained by quantitative evaluation of its gray scale profile.

Recording SEM micrographs and cross section profile analysis of the tested catalyst-coated membranes was carried out using a Zeiss Gemini 55 scanning electron microscope.

3. Results

3.1. Water accumulation in channels

Our micro PEFC shows unsteady behavior when flow fields in meander shape with parallel channels are employed. Irregular

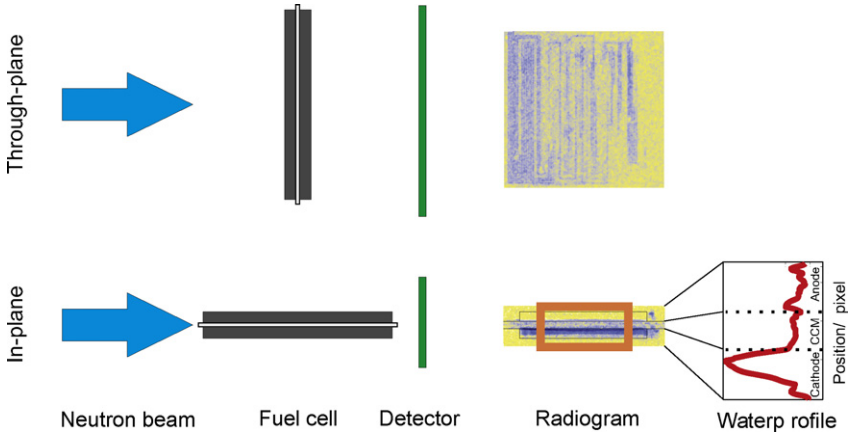

Fig. 1. Measurement principle for through-plane and in-plane neutron radiography on a GDL-less micro PEFC. For in-plane neutron radiography, the rectangle indicates the area that is analyzed to obtain a water profile.