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The influence of gas diffusion layer wettability on direct methanol fuel cell performance: A combined local current distribution and high resolution neutron radiography study

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ABSTRACT

The influence of the anode and cathode GDL wettability on the current and media distribution was studied using combined *in situ* high resolution neutron radiography and locally resolved current distribution measurements. MEAs were prepared by vertically splitting either the anode or cathode carbon cloth into a less hydrophobic part (untreated carbon cloth 'as received') and a more hydrophobic part (carbon cloth impregnated by PTFE dispersion). Both parts were placed side by side to obtain a complete electrode and hot-pressed with a Nafion membrane. MEAs with partitioned anode carbon cloth revealed no difference between the untreated and the hydrophobised part of the cell concerning the fluid and current distribution. The power generation of both parts was almost equal and the cell performance was similar to that of an undivided MEA (110 mW cm^{-2}, 300 mA cm^{-2}, 70 °C). In contrast, MEAs with partitioned cathode carbon cloth showed a better performance for the hydrophobised part, which contributed to about 60% of the overall power generation. This is explained by facilitated oxygen transport especially in the hydrophobised part of the cathode gas diffusion layer. At an average current density of 300 mA cm^{-2}, a pronounced flooding of the cathode flow field channels adjacent to the untreated part of GDL led to a further loss of performance in this part of the cell. The low power density of the untreated part caused a significant loss of cell performance, which amounted to less than 40 mW cm^{-2} (at 300 mA cm^{-2}).

1. Introduction

On the cathode side of a liquid fuelled DMFC, the flooding is more pronounced than in a PEFC, since the water is not only produced on the cathode side but permeates through the membrane additionally, driven by a concentration gradient and electroosmotic drag. On the anode side, the blocking effects of CO_2 bubbles may lead to a disturbance of the methanol supply. These two-phase flow effects do play a crucial role not only inside the GDL but also in the flow field channels. Due to the interaction between GDL and flow field, different GDLs result in altered fluid distributions inside the cell and therefore in different operating behaviours [1].

Uneven fluid distributions cause inhomogeneous current distributions which may lead to a significant power loss and accelerated degradation of the fuel cell. In order to investigate the effects leading to inhomogeneous current distributions, a measurement technique is mandatory, that allows the *in situ* observation of the current, CO_2 and water distribution simultaneously.

The use of segmented printed circuit boards (PCBs) is a well-established technique for measuring local currents in fuel cells. The features and advantages of our self-developed set-up, which is based on printed circuit board technology, are described in [2] (see also section 2). It allows the accurate measurement of up to 54 segment currents and impedances based on compensated sensor resistors [3].

Several methods have been reported in the literature to observe the CO_2 and water distribution *in situ* under operating conditions of PEFCs and DMFCs. Some authors used cells with a transparent cover to observe the carbon dioxide evolution and the two-phase flow behaviour visually. Transparent anode covers allow for the observation of different CO_2 flow patterns in DMFCs as a function of flow field design, current density, temperature, flow rate, pressure drop, and orientation [4–7]. A special set-up using a porphyrin dye compound reveals the distribution of oxygen in the cathode channels of a DMFC [8]. Observations of water transport phenomena in the cathode channels of PEFCs are also possible [9–11].

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A further method is synchrotron X-ray radiography [12–15]. This method allows the *in situ* observation of the fluid distribution in polymer membrane fuel cells on the micrometer scale with a resolution up to 3 μm. In the field of hydrogen fed PEFCs, the formation, growth and transport of water droplets have been studied [12–14]. Through-plane measurements of Manke et al. [12] proved the existence of different transport mechanisms: the first one via a continuous GDL pore filling, indicating a continuous "capillary-tree-like" transport, and the second one via an eruptive transport process. In-plane measurements of Hartnig et al. [13,14] enable a cross-sectional insight in the evolution and transport of water and thus a distinction between the different layers of the fuel cell. Both through-plane and in-plane techniques were applied to DMFCs under operating conditions [15]. The authors studied the carbon dioxide evolution and bubble formation at DMFC anodes. They found out that the dynamics of bubble formation and the detachment of bubbles from the position of formation strongly correlate with the current density [15].

In order to use a completely non-invasive method for the observation of CO_2 and water, we used neutron radiography which has proved its applicability for a variety of questions [16–22]. This method is based on the high attenuation coefficient of hydrogen compared to the attenuation coefficient of most metals and carbon. It means that the neutron beam can penetrate the metallic end plates and graphitic flow fields almost unattenuated, whereas liquid water leads to a strong attenuation of the beam. Thus, the distribution of hydrogen-rich species such as water and methanol can be observed during operation. Vice versa, areas where no liquid can be detected must be interpreted in terms of gas phase (air, carbon dioxide). In 1999, Bellows et al. used neutron radiography to study water transport profiles across Nafion in operating PEFCs [16]. Six years later, Kramer et al. investigated the two-phase flow inside the anodic compartment of an operating direct methanol fuel cell [17]. Manke et al. [18] presented a quasi-*in situ* neutron tomography on PEFC stacks including a cell-by-cell detection of liquid water agglomerates. A study of combined neutron radiography and locally resolved current density measurements of operating PEFCs was reported by Hartnig et al. [19]. They correlated the water distribution with the local activity of the respective area. In 2008, Manke et al. [20] investigated the liquid water exchange in two-phase flows within hydrophobic porous gas diffusion materials of PEFCs by spatially resolved hydrogen–deuterium contrast neutron radiography. Based on these results, they derived a new model for the water transport based on an eruptive mechanism. Hickner et al. [21] and Boillat et al. [22] carried out high resolution neutron radiography measurements using the in-plane imaging mode. They obtained detailed information on the cross-sectional water distribution in the MEA components and the gas flow channels. In our recent paper [23], the combination of *in situ* high resolution neutron radiography and segmented current distribution measurement was identified as a suitable tool to correlate current and fluid distribution in DMFCs. It was found that strongly inhomogeneous current distributions during cathodic flooding processes result in a performance loss of up to 30% of the initial value [23].

The intention of the present work is to study the influence of the anode and cathode GDL wettability on the current and media distribution using combined *in situ* high resolution neutron radiography and current distribution measurements. To visualize the difference between untreated and hydrophobised parts of the cell, either the anode or cathode GDL is vertically split into a less and a more hydrophobic part. The current distribution on the left and the right side of cells with undivided membrane electrode assemblies (MEAs) is approximately mirror-inverted, suggesting similar fluid distributions on the left and the right side of the cells. This is a condition precedent for the procedure of vertically splitting a GDL in two parts with a different hydrophobicity, because unequal current or media distributions on the left and the right part of the cell can be attributed to dissimilar hydrophobic properties of the two GDL parts. In contrast, a horizontal splitting of the GDLs would not be useful, since the media and current distribution of the upper and lower part of the cell is considerably different, caused by an accumulation of CO_2 in the top part of the cell and flooding in the middle and bottom part of the cell.

2. Experimental

2.1. Preparation of MEAs

The functional layers of the used MEAs with an active area of 4.2 cm × 4.2 cm were prepared onto carbon cloth (Ballard). The carbon cloth was used either as received or hydrophobised by impregnation with PTFE dispersion. Together with a microporous layer, the carbon cloths were used as gas diffusion layers for the electrodes. To compare hydrophobised and untreated GDLs in the same cell under operating conditions, either the anode or cathode GDL was vertically split into an untreated left part and a hydrophobised right part (see scheme in Fig. 1). To avoid an interaction of anode and cathode effects, the corresponding counter electrode was always undivided and hydrophobised.

As functional layers, first a hydrophobised microporous layer and then either the anode or cathode catalyst layer were prepared on the carbon cloth substrates by knife-over-roll technique. The microporous layer consisted of 60 wt.% carbon (Cabot, 2.1 mg cm^{-2}) and 40 wt.% PTFE (1.4 mg cm^{-2}). The anode catalyst consisted of 75 wt.% Pt/Ru and 25 wt.% carbon (Johnson Matthey). The Pt/Ru loading of the anodes was about 2 mg cm^{-2}. The cathode cata-

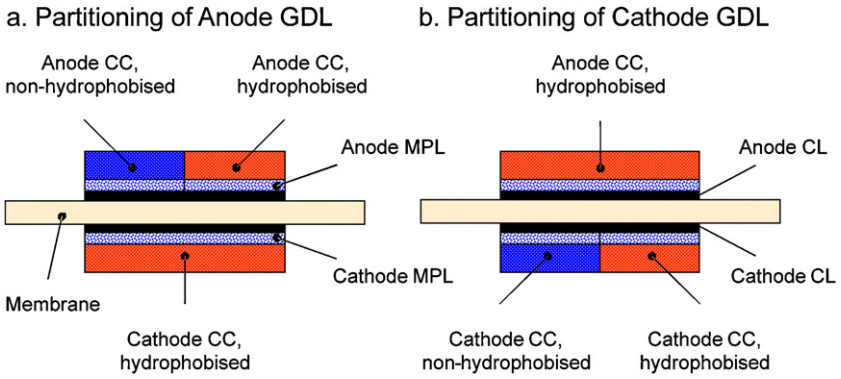

Fig. 1. Scheme of GDL partitioning by vertically splitting the carbon cloth into an untreated and a hydrophobised part. The neutron radiographs always represent the view from the cathode side. The splitting of anode and cathode was done in such a way, that the untreated carbon cloth always appears on the left hand side, and the hydrophobised carbon cloth is indicated in the right hand side of the neutron radiographs. *Abbreviations.* CC: carbon cloth; MPL: microporous layer; CL: catalyst layer.