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Combined Local Current Distribution Measurements and High Resolution Neutron Radiography of Operating Direct Methanol Fuel Cells

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1 Abstract

Neutron radiography allows the investigation of the local fluid distribution in direct methanol fuel cells (DMFCs) under operating conditions. Spatial resolutions in the order of some tens of micrometers at the full test cell area are achieved. This offers the possibility to study practice-oriented, large stack cells with an active area of several hundred cm^2 as well as specially designed, small test cells with an area of some cm^2. Combined studies of high resolution neutron radiography and segmented cell measurements are especially valuable, because they enable a correlation of local fluid distribution and local performance [1, 2]. The knowledge of this interdependency is essential to optimise the water management and performance respecting a homogeneous fluid, current and temperature distribution and to achieve high performance and durability of DMFCs.

2 Introduction

One of the main problems in the development of direct methanol fuel cells is the uneven fluid distribution. While CO_2 bubbles may inhibit the methanol supply on the anode side, water droplets on the cathode side block the oxygen supply. Combined with the concentration decrease of the reactants across the active area along the flow field channels, these effects lead to a pronounced inhomogeneous current distribution as well as to a power loss of the fuel cell. With the knowledge of the local distribution and transport behaviour of CO_2 bubbles and water droplets at different operation modes, investigations on the improvement of cell components and design are possible.

By means of segmented circuit boards, the currents of separate cell segments can be measured during operation of the cell. In order to investigate the effects leading to the inhomogeneous current distribution, a further measurement technique is mandatory, allowing the observation of the CO_2 and water distribution. 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 [3–10]. This method is based on the high attenuation coefficient of hydrogen compared to the attenuation coefficient of most metals and carbon. The neutron beam is less affected by the solid cell components compared to liquid water which leads to a strong absorption of the beam. Thus, the distribution of hydrogen-rich species can be observed during operation. In the test set-up, the neutron radiation is attenuated while passing the cell in through-plane direction. The transmitted radiation is converted into visible light by means of a scintillator which then can be detected by a charge-coupled device camera. Placing the scintillator close to the test cell allows for resolutions down to 70 µm. A combination of neutron radiography and segmented current distribution measurement results in an *in situ* correlation of the current and fluid distribution.

3 Experimental

3.1 Electrochemical set-up and test cell

The functional layers of the used membrane electrode assemblies (MEAs) with an active area of either 4.2 cm × 4.2 cm or 21 cm × 15 cm were prepared onto carbon cloth (Ballard). In case of the small MEAs, an untreated carbon cloth and a (standard) hydrophobised carbon cloth were used as substrate. To compare hydrophobised and untreated gas diffusion layers (GDLs) in the same cell under operating conditions, the cathode GDL was vertically split into an untreated left part and a hydrophobised right part. In case of large stack MEAs, only hydrophobised carbon cloth was used. The microporous layer consisted of 60 wt.% carbon (Cabot) and 40 wt.% PTFE. 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 catalyst had a composition of 57 wt.% Pt and 43 wt.% carbon (Johnson Matthey) with a Pt loading of about 2 mg cm^{-2}. The anode and cathode electrodes were hot-pressed on both sides of a Nafion N-115 membrane.

Two types of flow fields were used: The first type of flow field is made of graphite and is used for the electrodes of small cells with an active area of about 18 cm^2. These flow fields have a grid design with ribs (1 × 1 mm^2 area) and channels (1 mm width and depth). The second type of flow field is made of Sigraflex (SGL Group) and applied for the electrodes of large stack cells (active area: 315 cm^2). The anode flow field has a 6-fold meander design and the cathode flow field a multi-channel design. The flow arrangement of all the flow fields was counter flow. The air feed was at the top and the methanol feed at the bottom of the cells.

All measurements were carried out at a temperature of 70 °C and ambient pressure. The anode was constantly fed by a methanol solution with a concentration of 1 mol l^{-1} and the cathode was supplied by air. The respective stoichiometric factors are indicated in the figures below.

The current distribution was measured via segmented printed circuit boards (PCBs) which were inserted between the aluminium end plate and one of the flow fields. An exploded view of the assembly used for small cells is shown in Fig. 1. A detailed description of the setup can be found in [11]. Adapted to the flow field sizes, circuit boards with either 25 segments (small cells) or 54 segments (stack cell) were used.

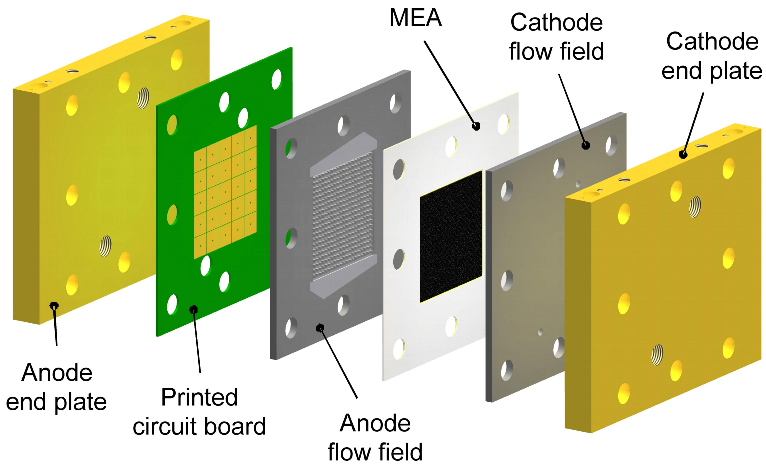

Figure 1: Exploded assembly drawing of the test cell including the adapter printed circuit board (PCB) used in [1, 2].

3.2 Neutron radiography

The radiography experiments were performed at the neutron tomography instrument CONRAD/V7 at Helmholtz Centre Berlin (formerly Hahn-Meitner Institute) in Germany. The imaging set-up is based on a pinhole geometry with a small variable aperture. The main part of the detector system is a 16-bit low-noise CCD camera (Andor DW436N with 2048×2048 pixel^2) 0. The camera is focused by a lens system on a neutron sensitive scintillator screen (mostly Gadox or LiF) which was mounted close to the fuel cells to ensure high spatial resolutions down to 70 µm in case of the small cells and 200 µm in case of the large cells.

4 Results of Combined Neutron Radiography and Current Distribution

The results obtained with a small MEA including a cathode carbon cloth splitted into an untreated part (left side of cell) and a hydrophobised part (right side of cell) are shown in Fig. 2. The left part of Fig. 2 shows the neutron radiograph and the right part the corresponding current distribution for an average current density of 300 mA cm^{-2}. Under these conditions, water droplets appear in the cathode channels over the entire left side of the cell. The flooding of cathode channels (see dark spots on neutron radiograph) corresponds to the decreased local current in this part of the cell (see blue segments): The untreated part of the cell contributes to 38 % of the total power generation only.

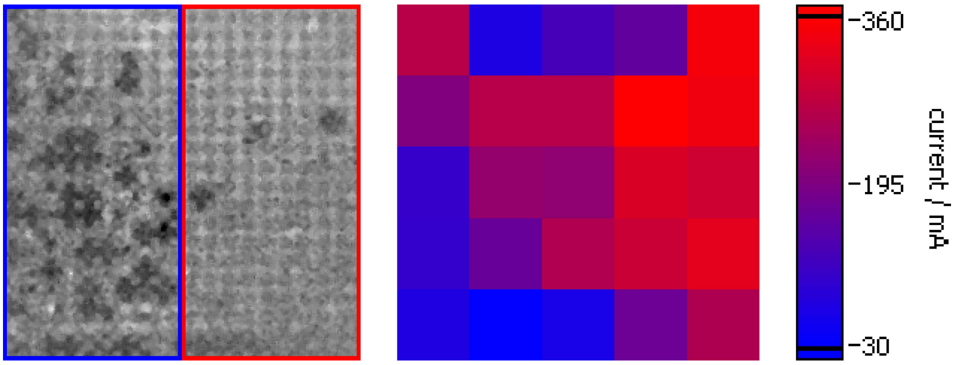

Figure 2: Normalised radiograph (left hand) and the corresponding current distribution (right hand) of a MEA with a vertically split cathode carbon cloth; T = 70°C, $\lambda_{MeOH} = \lambda_{air} = 4$, j = 300 mA cm^{-2}; dark spots in cathode grid channels indicate water droplets; light grey colour of anode grid channels reveals CO_2 evolution.

At the neutron tomography instrument CONRAD/V7 at Helmholtz Centre Berlin, a neutron beam widening allows to investigate areas up to 20 cm × 20 cm. This area is for example adequate for large single stack cells of Forschungszentrum Jülich GmbH with an area of 315 cm^2 (21 cm × 15 cm). The design of these stack cells includes a multifold-meander anode flow field and a multi-channel cathode flow field. Fig. 3 shows a first, normalised neutron radiograph of such a stack cell under DMFC operating conditions (T = 70 °C, j = 150 mA cm^{-2}, $\lambda_{air} = \lambda_{MeOH} = 4$). Though the distribution of the neutron beam intensity is locally and temporally inhomogeneous and has to be improved further, the light grey meander channels and water droplets in parts of the cathode channels can be clearly identified (left hand of Fig. 3). The current distribution shows a lower power generation of 39 % in the bottom part of the cell (right hand of Fig. 3), which is most probably caused by oxygen depletion. It is assumed, that the oxygen concentration in the bottom part of the cell is not only reduced by consumption due to Faradaic reaction, but also by partial blocking of cathode channels.

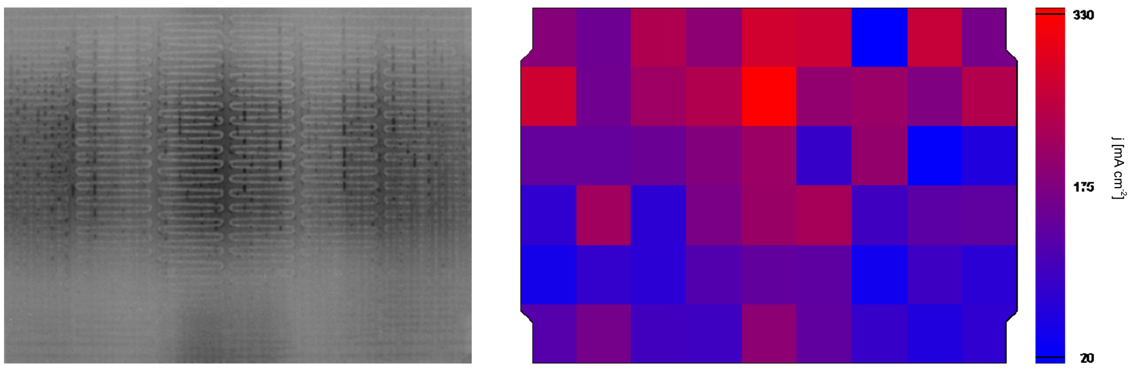

Figure 3: Normalised radiograph (left hand) and the corresponding current distribution (right hand) of a single stack MEA (active area: 315 cm^2); T = 70 °C, $\lambda_{MeOH} = \lambda_{air} = 4$, j = 150 mA cm^{-2}; dark spots in cathode straight channels indicate water droplets; light grey colour of anode meander channels reveals CO_2 evolution.

5 Conclusions

The combination of high resolution neutron radiography and simultaneous measurement of the local current distribution provides valuable information about the influence of GDL wettability on the performance of a DMFC. It turns out that hydrophobisation of the cathode carbon cloth seems to be important, as it enables a fast removal of water droplets, facilitates the oxygen transport in the cathode GDL and cathode flow field channels and thus increases the performance. It should be emphasised, that a simulation of the flow conditions in large stack cells by using small single cells is challenging. Hence, for future neutron radiography measurements in through-plane mode one should pay special attention to the investigation of practice-oriented, large stack cells. For the first time, the fluid distribution of large stack cells was measured by combined neutron radiography and current distribution measurements.

Acknowledgements

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