μPIV measurements of the CO₂-bubble evolution in the anode flow of an operated direct methanol fuel cell

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Abstract In direct methanol fuel cells (DMFCs) two-phase flows appear in the channels of the anode side as well as of the cathode side. At the cathode side water droplets appear in an ambient air flow whereas at the anode side CO₂-bubbles emerge in a liquid water-methanol environment. The assembly of the porous gas-diffusion layer (GDL) between the channels and the membrane complicate that flow phenomenon even more. CO₂-bubbles or water droplets may almost completely fill the cross section of a channel. CO₂-bubbles tend to form slugs that eventually move through the channel. The effect of two-phase flows on the cell performance has not been investigated in detail yet. In the current project the micro-Particle-Image-Velocimetry (µPIV) technique is used to elucidate the corresponding flow phenomena on the anode as well as on the cathode side of a DMFC and the performance of the cell. The first part of the project is the investigation of the anode side. Hence, a single-channel DMFC is constructed that allows for µPIV measurements at the anode side as well as a detailed time-resolved cell-voltage recording. The flow inside the anode-channel as well as the bubble clogging and slug movement is investigated avoiding a flow shortcut through the GDL between neighboring channels as in serpentine or parallel-channel configurations. Optical access is granted to the anode side by a transparent foil. Fluorescent tracer particles are added to the water-methanol flow. The particles are illuminated and their movement is detected using a microscope. The appearance and evolution of CO₂-bubbles is qualitatively and quantitatively investigated. The analysis of the velocity distribution around a CO₂-bubble or a moving slug allows a deeper understanding of the coherence of fluid motion, channel blockage and cell performance. Additionally to the µPIV measurements a time-resolved recording of the cell-voltage is performed. The results clearly indicate that the cell power increases when the free cross-section area of the channel is decreased by huge bubbles. Methanol is forced into the GDL, i.e., methanol continuously is convected to the catalyst layer and is oxidized to CO₂. Hence, the fuel consumption is increased and the cell performance rises. When the huge bubble is released from the GDL and forms a moving slug, the moving slug effectively cleans the channel from CO₂-bubbles on its way downstream. Since the channel cross section is not severely diminished by the bubbles at this stage, the methanol flow is not forced into the GDL anymore. The remaining amount of methanol in the GDL is oxidized. The cell power decreases until enough CO₂ is produced to eventually form bubbles again that significantly decrease the free cross-section of the channel and the process starts again.

1. Introduction

Due to their high energy density methanol operated fuel cells will play an important role for portable electronic devices and will compete with batteries in the near future. A direct methanol fuel cell (DMFC) consists of an anode and a cathode current collector plate which contain flow channels for the supply of fuel and oxidant, respectively. The adequate distribution of the reactants is directly related to the cell voltage and cell power [4]. Typically, micro-channel structures are used. Between those plates a membrane serves as the electrolyte and separates the reactants. On each side of the membrane a catalyst layer is applied, followed by a so called gas diffusion layer. This GDL usually consists of carbon fibers, i.e., the GDL forms a porous layer. The electrochemical reaction is as follows:
In DMFCs two-phase flows appear in the channels of the anode side as well as in the channels of the cathode side. At the cathode side water droplets appear in an ambient air flow whereas at the anode side CO$_2$-bubbles emerge in a liquid water-methanol environment. The assembly of the GDL between the channels and the membrane complicate that flow phenomena even more. CO$_2$-bubbles or water droplets may almost completely fill the cross section of a channel. CO$_2$-bubbles tend to form slugs that eventually move through the channel. It is known that slight changes of the fluid motion and distribution may lead to severe changes of the cell performance (Li and Sabir, 2005). The water management of fuel cells, especially of proton exchange membrane fuel cells (PEMFC), is one of the main problems in current fuel cell research. Additionally, for a DMFC, the appearance of CO$_2$-bubbles is supposed to significantly alter the cell performance. However, although the performance of a fuel cell is directly linked to fluid mechanics a detailed overview of those aspects are rare: the review of Li et al. (2008) concerning the water management and water transportation phenomena needs to be mentioned as well as the report of Bazylak (2009) which deals with the visualization of liquid water in PEM fuel cells. Kejiang et al. (2009) present an overview about microfluidic fuel cells, also reviewing mixing aspects. In the current project the corresponding flow phenomena on the anode as well as on the cathode side of a DMFC are to be investigated by the micro-Particle-Image-Velocimetry ($\mu$PIV) technique. The first part of the project is the investigation of the anode side.

As mentioned above, CO$_2$-bubbles at the anode side of a DMFC are believed to have a negative effect on the cell performance. Some groups tried to visually analyze the appearance and evolution of CO$_2$-bubbles in DMFCs that provide optical access. Argyropoulos et al. (1999) and Liao et al. (2007) investigated the CO$_2$-bubbles in a DMFC with parallel channels and observed channel-filling slugs. Both papers related a better cell performance with a higher overall volume flow, i.e., a better slug transport. A similar configuration with parallel channels was analyzed by Lu & Wang (2004). They found that hydrophilic GDLs lead to small bubbles that are easy to remove whereas for hydrophobic GDLs large channel filling slugs emerged. A single-serpentine channel design was investigated by Yang et al. (2005). They observed more and larger bubbles at higher current densities and smaller bubbles and higher methanol cross-over from the anode to the cathode side at increased volume flow rates. However, in all these investigations the cell performance was only globally validated. The instantaneous influence of the bubbles and slugs on the cell performance could not be investigated since time-resolved voltage measurements were not performed. The question rises whether an increased cell performance is related to a better slug transport or is simply caused by an increased amount of fluid flow through the GDL when the volume flow rate is increased. In the current work fluid mechanics and cell performance will be investigated synchronously using $\mu$PIV and a time resolved voltage measurement.

As can be seen from the literature presented above, fluid mechanics just recently came into focus of fuel cell research. The same applies for flow measurements. A review of the application of laser-optical measurement techniques to fuel cells is presented in Lindken et al. (2012). PIV (Particle Image Velocimetry) measurements that elucidate some fundamental phenomena of a fuel-cell related flow field or manifold have been performed by Martin et al. (2005), Feser et al. (2007) Lebaek et al. (2010) and Klinner et al. (2011).

In the present work $\mu$PIV is applied. Details about this method can be found in Lindken et al. (2009) and Wereley and Meinhart (2009). $\mu$PIV is not widely used in fuel cell research due to seeding problems in micro-gas-flows. Some publications have to be mentioned: Sugii and Okamoto

$$\text{anode side: } CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$$

$$\text{cathode side: } 1/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$

$$\text{DMFC reaction: } CH_3OH + 1/2O_2 \rightarrow 2H_2O + CO_2$$ (1)
(2006) and Yoon et al. (2006) performed µPIV measurements in a gas-flow in fuel-cell-like micro-channels. The seeding was provided by fluorescent olive oil droplets in the first case and by smoke particles and water droplets in the second case. However, the absorption of oil particles in the GDL, the disturbance of the water management or the damage of the membrane by smoke particles would lead to a decrease of the cell performance if used in a real operating fuel cell. We presented an alternative seeding for µPIV in fuel-cell-like micro-channels in Burgmann et al. (2011): atomizing ethyleneglycol with Rhodamine-B seems to be a suitable way since those particles adequately follow the flow and emit sufficient fluorescent light. Recent measurements at the cathode side of an operating DMFC using such a seeding proved that the cell performance is not altered by those particles. This investigation is the basis for the second part of the current research project, i.e., the measurement of the two-phase flow at the cathode side of a DMFC. In this paper the results of the first part are reported which is the measurement at the anode side of a DMFC, i.e., gas-bubbles in a liquid environment. Further details on the results of this research project can be found in Burgmann et al. (2012).

Although µPIV in liquids is easy to achieve to our knowledge there are only two groups who used this technique in a fuel cell related context. The first publication is from Minor et al. (2008). A water droplet with premixed particles was artificially injected into a micro-channel with a real GDL to analyze the droplet deformation and contact angle hysteresis. The second work was performed by van der Schoot et al. (2008) and deals with to the fluid motion in the channels of a DMFC at operating conditions. The CO₂-bubble growth at the anode side was analyzed for different volume flow-rates of the methanol-water mixture. The current paper presents a continuation of that work.

2. Measurement set-up

As mentioned above in this work µPIV measurements are performed to investigate the flow phenomena within the anode-channel of a DMFC when bubbles and slugs appear. The µPIV set-up consists of a Zeiss Axio-Observer Z1 epi-fluorescence microscope with a 12 bit PCO Sensicam QE and a Newave Pegasus frequency doubled Nd:YLF laser. The water methanol flow was premixed with FluoRed tracer particles with a diameter of 1.22 µm. The particles are illuminated with green laser light, start to fluoresce and emit red light. A dichroic mirror within the light path separates the particle light from the (green) background light. The measurement plane is defined by the focal plane of the microscope lens. The effective magnification of the system is M = 3.15. Davis 7.2 PIV software from LaVision is used to perform the pre-processing of the raw images and the PIV evaluation of the particle images by cross-correlation schemes.

A single-straight-channel configuration was chosen for the DMFC design in this work. Using such a configuration parasitic effects like flow short-cut through the GDL between neighbouring channels, as in serpentine or parallel-channel configurations, can be avoided. Hence, the coherence between the bubble growth and transport and the cell performance can be directly measured. In most cases there is just one slug moving through the channel at a certain time-stamp. The channel of the anode side as well as of the cathode side is a 55 mm long channel with a cross section of 1×0.67 mm². An area of 2.8 × 2.1 mm² (region of interest, ROI) can be observed by the microscope, since the anode channel is open and covered with a transparent foil. The GDL is a woven carbon cloth which has a hydrophobic surface. Thermo-foils are attached to the anode and the cathode plate, respectively, to adequately heat the cell. The water methanol mixture at the anode side is preheated using a heating hose. PT100 thermo-sensors are integrated in the cell to control the temperature level of the cell. A sketch of the design of the DMFC is given in fig. 2. Further details on the design and components of the DMFC can be found in Burgmann et al. (2012).
The performance of a DMFC depends on several parameters like temperature, molar fraction of methanol in water, volume flow rate etc. We initially performed several tests on those parameters qualitatively observing the bubble appearance and slug transport. Since the cell voltage measurement is not segmented yet, we chose a parameter set which only allows a single slug in the channel at a certain time step. Hence 2 mol/l methanol in water where used at a flow rate of 0.5 ml/min leading to a Reynolds number of $Re=14.8$. A syringe pump is used to feed the cell. Air flow rate at the cathode side was set to 150 ml/min. Cell temperature was set to 70°C. The current density was varied. Fig. 2 shows the measurement set-up in the laboratory.

3. Results

The cell power and cell voltage depends on the current density. At low current density the cell performance is governed by reaction kinetics such that the cell voltage drops strongly until a stable regime is reached. At high current densities transport-limitation effects dominate such that the cell voltage significantly drops again. The peak power density corresponds to the linear part of the characteristic curve. In this regime the transport of electric charge governs the performance of the
cell. The characteristic curve of the DMFC used in this work is shown in fig. 3 with normalized values for current density, voltage and power. Bubbles and slugs appeared for all levels of current density but changed in size and type of appearance.

![Characteristic Curve of DMFC](image)

**Fig. 3:** Characteristic curve of the DMFC indicating the typical slug conditions and the volume of CO\(_2\) transported by the slugs

At low current densities the bubbles are likely to appear at the corners that are formed by the channel walls and the GDL surface. Those bubbles grow and may finally almost completely cover the channel cross-section. One of those bubbles may break adrift and form a moving slug. With increasing power density the bubble pattern changes: more bubbles directly emerge from the GDL at the center of the channel. Those bubbles grow faster than the corner-bubbles and are candidates for forming a slug. At current densities larger than the peak power current density more bubbles appear at the center of the channel and may form some kind of chain of bubbles. Those bubbles may unite and form a slug. Under all conditions the slugs that are formed drift downstream with a speed lower than the bulk velocity of the flow. On their way downstream they collect all or most of the bubbles still sticking to the channel walls or the GDL. In other words the slugs lead to a cleaning of the channels. After a slug has passed bubbles appear and grow again most likely at the same position as before. The amount of CO\(_2\) that is transported out of the channel can be roughly calculated based on the slug length. The highest amount of CO\(_2\) is transported at the peak power density as indicated in fig. 3. Roughly the characteristic curve can be divided into 3 sections: at lower current densities few and small slugs appear. At higher current densities more slugs appear that have a medium size whereas at highest current densities only few slugs appear that are very large as indicated in fig. 3. Note, the amount of images recorded by µPIV is not sufficient for a detailed statistical investigation. However, the trends can be clearly seen.

![ Photograph of the Channel](image)

**Fig. 4:** Photograph of the channel showing bubbles and a moving slug
The region of interest (ROI) of the µPIV measurements was placed in the mid-section of the channel as indicated in fig. 4. In most cases the slugs are formed upstream of the ROI such that the passage of a slug and the corresponding cleaning of the channel can be analyzed. The results presented herein have been recorded at current densities around or below the peak power density. The sequence shown in fig. 5 exemplarily shows the bubble growth and the corresponding velocity distribution at the center plane of the channel (some more snapshots of the flow field can be found in Burgmann et al. (2012)). As can be clearly seen the bubble growth leads to an almost complete blockage of the channel cross section. Due to the ton-like or spherical shape of the bubbles only small areas at the top wall are kept free. However, the measured velocity increase is not as high as could be expected, i.e. only doubled velocities are recorded. This indicates a highly three-dimensional flow field.

![Fig. 5: Typical sequence of a bubble growth process and the slug passage at medium current densities](image)

For some selected cases the position of measurement plane was changed to further elucidate the flow around the bubbles and slugs. Some of those cases are depicted in fig 6. As can be clearly seen, in fig. 6a) some jet-like flow structures appear downstream of a bubble in a measurement plane close to the channel wall due to the blockage of the channel cross-section. The same phenomenon can be observed for measurement planes close to the GDL surface. In fig. 6 b) the rear part of a bubble, i.e., the upstream part of the bubble, is shown in a measurement plane close to the GDL surface. The measurement of the flow was partly done through the bubble since this bubble shows a wedge-like shape at this end. As can be seen the velocities increase under this triangular form at the end of the bubble. Note, the change of the optical path, i.e., the refractive index, may not lead to such a large difference. Obviously, the flow is deflected toward the GDL. This specific bubble is about to loose contact with the GDL and will form a slug.
Simultaneously to the \( \mu \)PIV measurements the cell voltage has been recorded. With the optical measurement technique the passage of a slug can be clearly identified such that changes of the cell voltage can be directly related to the passage of a slug. Interestingly, the measured velocities increase just before a slug is passing the ROI. This velocity increase appears over the complete measurement plane, i.e., it is not just a local velocity increase as those depicted in fig. 6a) for the jet-like velocity pattern. The analysis of the corresponding time-resolved voltage measurements shows a noticeable rise of voltage/power before the slug passes. After the slug has passed, the cell voltage decreases to a certain level and after a while increases again. Such a behavior is shown in fig. 7. The time the slug is passing the ROI is indicated for each depicted case. Obviously there seems to be a link between the slug and the temporal evolution of the cell-voltage. Usually a slug, which is in most cases formed upstream of the ROI is passing the channel length in 5 to 10 seconds. The slug velocity has been roughly measured to be 4 to 8 mm/s. Slugs that pass the ROI can be assumed to be formed just seconds ago upstream of the ROI.

Fig. 6 a): Flow around a bubble close to the top channel wall downstream of the bubble, b) flow at the upstream part of a bubble at a plane close to the GDL surface.

Fig. 7: Selected sequences of the measured velocity in the anode channel over time showing the passage of a gas-slug and the proceeding velocity increase (top), corresponding sequence of the measured normalized \( U(t) \) (bottom).
4. Discussion and conclusion

As has been shown growing bubbles significantly decrease the free cross-section area of the channel. Note, the volume flow rate that is set by the syringe pump is kept constant during the μPIV measurements. Hence, a blockage leads to a significant velocity increase as observed. However, the local increase is not as strong as could be expected, e.g., although the free cross section is only about 10% of the channel cross section, the locally measured velocities only double. This hints a strong three-dimensional velocity field. Furthermore, as can be deduced from observations as presented in fig. 6, bubbles lead to a stronger flow though the GDL. Usually the free cross-section within the porous structure is significantly lower than that of the channel. Channel-blocking bubbles decrease that ratio such that more fluid is supposed to pass through the GDL. Hence, additionally to the diffusive transport within the GDL a convective transport takes place leading to a stronger feeding of the catalyst layer below the GDL with fuel. A better performance of the cell can be concluded. This effect can be measured as demonstrated in fig. 7. Note, almost the complete channel is covered with growing bubbles. All those bubbles have a displacement effect on the flow. During this growing process, feeding of the GDL and the catalyst layer is improved such that the cell voltage increases. Finally, a slug is formed that moves downstream and that is cleaning the channel from remaining bubbles. Since the ratio of free cross-section of the channel and the GDL increases again the methanol within the GDL reacts and is not strongly replaced by fresh methanol as before. The cell voltage drops. However, the reaction is not completely stopped such that bubbles emerge again and the process starts again.

The velocity increase just before a slug is passing the ROI is not completely understood. As mentioned before, this increase appears over the complete width of the channel within the ROI. Hence, it is not a local effect due to some kind of jet-like structure that has been measured. The slugs travel with 4 to 8 mm/s which is lower than the bulk velocity of the flow. Fluid is forced through the corners between the channel walls and the slug and maybe through the GDL below the slug. Downstream of the slug a complicated 3D-flow structure may appear that may lead to the measurement of an in-plane velocity increase. The velocity increase is not due to an unstable behavior of the syringe pump. Unfortunately, although the bubbles tend to grow at the same position as before when a slug has passed, it was not possible to scan the flow across the channel height to reconstruct a phase averaged flow field. Such a scanning procedure is part of the current investigation.

However, some statements on the coherence of flow and cell performance can be concluded from this work: the negative effect of CO₂-bubbles on the cell performance which is often mentioned in literature is not a general property of those bubbles. As demonstrated in this work due to growing bubbles an increase of the cell voltage appears. This is explained by the displacement effect of those bubbles on the flow and the consequent forced convective transport in the GDL. Still some aspects need to be analyzed. The hydrophobicity and porosity of the GDL are supposed to have a significant effect on the two-phase flow structure and the cell-performance. Furthermore, methanol cross-over from the anode to the cathode side is forced when liquid water appears on the cathode side due to concentration gradients. The effect on liquid water, i.e., droplets at the cathode side on the cell performance will be investigated in the second part of the current research project. It has been demonstrated that seeding of micro-gas-flows is possible (Burgmann et al. (2011)). Recent investigations additionally demonstrated that the seeding material (ethylene-glycol with a mean diameter of 1μm) does not alter the cell performance. A segmented cell voltage measurement technique will also help in understanding the coherence of two-phase flow phenomena and cell performance.
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