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# On-line In-situ Diagnostics of Processes within PEM Fuel Cells by the Application of a Raman Fiber Technique

**Hans Bettermann**, **Peter Fischer**, Institut für Physikalische Chemie, Heinrich-Heine-Universität Düsseldorf, Düsseldorf, Germany

## 1 Introduction

In the recent years various physico-chemical methods have been considered to study fuel cells in operation [1]. These methods dominantly record global electric parameters. Apart global setups, segmented cells have been implied to monitor local parameters as for instance current densities or the distribution of temperatures.

This contribution intends to show how processes within PEM fuel cells can be locally resolved by applying Raman spectroscopy.

A striking advantage of Raman spectroscopy is its unpretentiousness concerning sample design and sample preparation. This enables measurements at hardly accessible locations. Furthermore, the Raman method is less interfered by water. Beside these two general conditions Raman spectroscopy belongs to the few methods that are able to analyze homo-nuclear diatomic gases or mixtures of them quantitatively [2,3]. This later property predestines the application to the pursuance of processes in which hydrogen and oxygen are involved. In the past, Raman spectroscopy has been applied to investigate degradation processes of membrane materials [4] as well as to detect intermediates on SOFC cermet anodes [5, 6].

A common drawback in applying Raman spectroscopy is however the small size of Raman cross sections. This property in general yields only weak light scattering signals especially for measuring trace-like samples as for instance gases in small sample volumes. The lack can be surmounted by using strong light sources, units with high throughputs of light, well chosen optic imaging conditions, and very sensitive detectors.

This contribution presents two experimental setups that make use of such components. The first setup that first demonstrates the feasibility of applying Raman spectroscopy for studying processes inside fuel cells combines a self-constructed Raman microscope with a suitable model fuel cell. The first concept of looking inside the fuel cell was then extended to an approach which allows the simultaneous detection of Raman spectra from seven points of a flow field canal. The issue of this experimental approach is to provide long-time measurements for pursuing local and global processes.

## 2 Experimental

The selected microscope objective let pass laser light (e.g., 458 nm, 100 mW) into the flow field and collects the generated Raman emission that is then dispersed by a spectrograph and detected by CCD-camera (cooled by liquid nitrogen, kept at -100 C°). A part of the experimental setup is shown in Fig. 1. The setup permits the record of hydrogen, oxygen, nitrogen, liquid water, as well as water vapor.

After proving the detectability of gases within the flow field by Raman spectroscopy, it was verified that the laser excitation does not interfere the fuel cell processes. Possible interferences are the local heating-up of flow field gases and the deterioration of the bipolar plate material by focused laser light. The polypropylene-graphite composite did not show any visual indication of damages after irradiation with intense laser light.

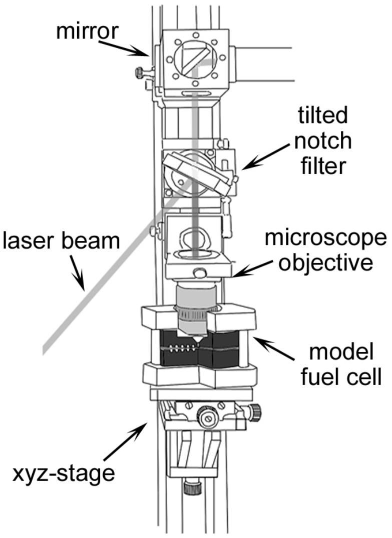

**Figure 1: Central part of the Raman microscope setup.**

A potential heating-up of gaseous samples can be directly proven by measuring the Raman signals of gaseous water quantitatively. The measurements showed that setting the laser power up to 1 W a temperature increase could not be identified.

The first concept of looking inside the fuel cell was then extended to an approach that allows the simultaneous detection of Raman spectra from several points of a flow field canal (single serpentine). The setup permits the simultaneous record of gas flows, liquid water and water vapor and how those species do change locally during operation. This was realized by a multiple-fiber Raman spectrometer with seven twin fibers. Each excitation fiber directed the laser beam to a specified position of the flow field. The beam of a frequency-doubled thin disk Yb:YAG laser (515 nm, 14 W) was coupled into the excitation fibers (multimode-step-index), respectively, focused by a micro lenses assembly and guided through small holes (1 mm) into the flow field canal. A second fiber attached to each excitation fiber collected the scattered light via the micro lenses and transmitted the Raman emission to the detection unit. The Raman light was again dispersed by a spectrograph and recorded by a CCD-camera. This setup permitted the record of spectra in a few minutes.

The fuel cell was part of a test station that was designed and manufactured by the German Aerospace Center (DLR, Stuttgart, Germany). The test station comprises the control of the humidification, the temperature of the fuel cell and the humidifiers, gas flows and pressures on both the anode and cathode side. Two separate humidifiers externally humidified the gases. The fuel cell was operated in a constant voltage mode. Gas flows were set to the stoichiometric factor of 1.5 for a current density of 1 A $cm^{-2}$.

## 3 Results and Discussion

The first setup was used to study membrane damages by Raman microscopy. For this, an artificial hole was manufactured within the Nafion™ membrane by aligning the laser focus onto the MEA surface for a short time. The following Raman spectra exhibited the passage of $N_2$ and $O_2$ from the cathode to the anode as well as the generation of water by a catalytic oxidation of $H_2$ at the rim of the hole. A strong local increase of temperature next to the membrane hole was identified by measuring changes of the intensity distribution of rotational $H_2$-Raman bands.

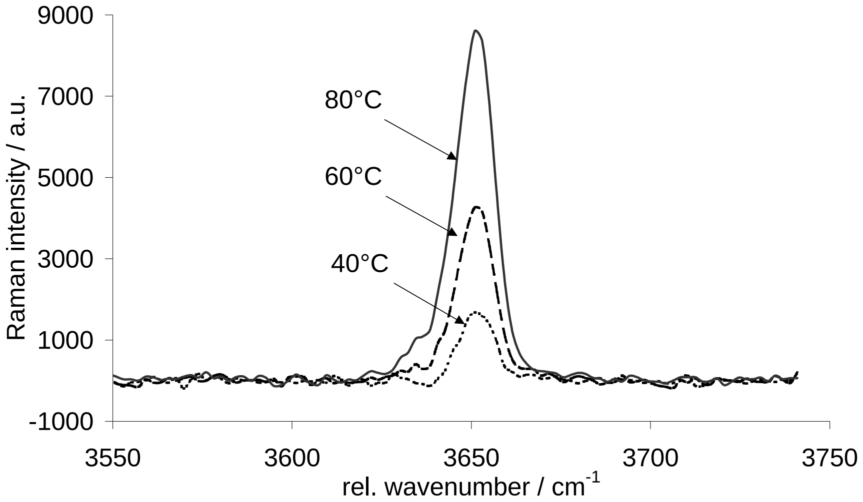

**Figure 2: The water vapour signal at different temperatures, Q-branch of the totally symmetric OH stretch mode, centre of signal: 3652 cm$^{-1}$; excitation wavelength: 477 nm, laser power 1 W, exposure time: 10 min.**

Water vapor inside fuel cell canals is more difficult to measure than gases because at low temperatures the mole fraction of gaseous water amounts only few percent of the gas mixture. For this reason, measurements of water vapor at room temperature require stronger laser powers (> 1 W). The Raman signal of water vapour (Q-branch of the totally symmetric OH stretch vibration with highest signal intensity) at different temperatures is presented in Fig. 2.

Detailed information concerning the local conditions of gases especially within the anode canal were achieved by the multi-fiber setup.

The Raman measurements at each measuring point within the anodic flow field exhibited considerable time-dependent fluctuations of hydrogen density. The fluctuations of the $H_2$ concentrations are addressed to the changing flow conditions inside the flow field as a result of the humidification of the anode. A direct relation between fluctuations of hydrogen density and fluctuations of the cell power could be observed next to the entrance of the anode flow field. Cell power fluctuations occurred after longer operation times. At the end of the anode meander phase shifts between the fluctuations of the hydrogen signal and those of the power signal were observed as an additional result of humidification. Since droplets are moved by the gas flow, the cross section of the canal is therefore altered locally and the $H_2$ flow passes several bottlenecks.

Heating the cell at 75 °C, Raman signals of water vapor were observed (Fig. 3). The spectra first revealed an increase of water vapor with increasing canal length.

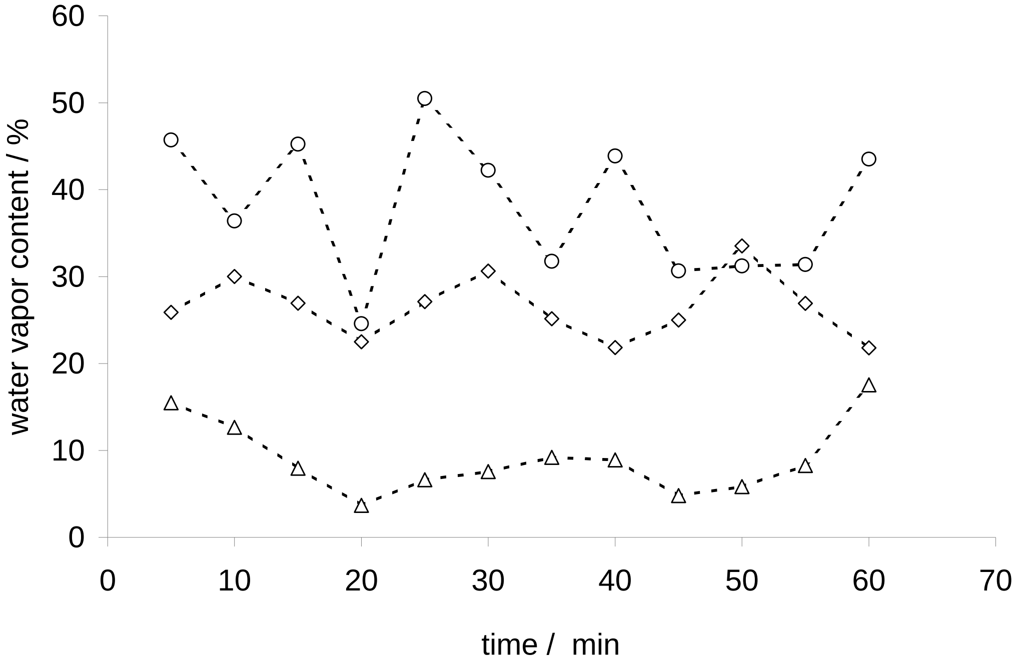

**Figure 3: Evolution of the absolute humidity (water vapour signal: 3652 $cm^{-1}$) as a function of time at three different ports along the anode meander; cell temperature: 75 °C; lower track: port next to the entrance, central track: port close to the center of the canal, upper track: next to the exit of the canal.**

This could be directly seen from the average values of water vapor obtained from the selected measuring ports. Time-dependent fluctuations of water vapor did also occur. The local fluctuations of water vapor are obviously coupled to the local condensation of water in almost the same manner as it has been found for the changes of hydrogen concentration.

The spectra also show that the time periods in which changes of water concentration take place become shorter with increasing canal length. Condensation occurs primarily at the end of the meander since the atmosphere of the canal enriches with water vapor. Condensation leads to a temporary contraction of the cross-sectional canal area or its complete blockage. Both obstructions may cause an increase of pressure just in front of the water droplets.

The local Raman spectra were compared with local current density measurements and global impedance spectroscopy. Beside the collection of data for modelling fuel cell processes, the multiple-fiber setup is primarily considered to monitor degradation processes and pre-stages of membrane damages. This project is part of a close cooperation with the DLR (German aero space center, Stuttgart, Germany) and the ZBT (center for fuel cell technology, Duisburg, Germany).

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