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Spatially Resolved Impedance Spectroscopy in PEM Fuel Cells up to 200 °C

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1 Introduction

Electrochemical impedance spectroscopy (EIS) is widely used to separate different loss mechanisms in fuel cells due to their different time constants [1]. It is mostly difficult to interpret and valuate the different phenomena by the analysis of the overall current density and cell impedance. Conducting spatially resolved EIS combined with local current density measurements enables the localisation of these different loss mechanisms and degradation phenomena. Additionally the local detection of e.g. fuel starvation or flooding events can help to understand the cell behaviour at critical operating states. Spatially resolved characterisation in combination with electrochemical impedance spectroscopy of conventional PEM fuel cells has been carried out earlier by Hakenjos et al. [2].

The high temperature polymer electrolyte membrane (HTPEM) fuel cell based on phosphoric acid doped polybenzimidazole (PBI) membranes was primarily developed by Wainright et. al. [3] in the middle of the 1990s. Due to several significant advantages they are a promising fuel cell technology and are nowadays receiving growing attention in research. The key advantage is the higher operation temperature of 120 °C to 200 °C compared to conventional low temperature PEM fuel cells based on Nafion® membranes. These operating conditions can be achieved due to a higher chemical and thermal stability of PBI and a proton conducting mechanism that does not require liquid water. The operating temperature leads to a more useful waste heat, a simplified system design due to the easier water management and, above all, to a significantly higher tolerance against catalyst poisons like carbon monoxide [4, 5]. Therefore, the most favourable application for HTPEM fuel cell systems is a combined heat and power (CHP) system in combination with a reformer unit.

In this work, a sophisticated experimental setup for spatially resolved characterisation of conventional and high temperature PEM fuel cells available at the Fraunhofer ISE is described in detail as well as the in-house designed and manufactured test cell. Exemplary some results of spatially resolved measurements are presented to demonstrate the opportunities of the described test facility. The influence of gas stoichiometry on the lateral distribution of current density in a HTPEM fuel cell was investigated at an operating temperature of 160 °C and a cell voltage of 0.5 V. Additionally, impedance spectra at selected cell segments are presented for deeper analysis of the spatial variety of the present processes.

2 Experimental Setup

At the Fraunhofer Institute for Solar Energy Systems ISE a custom-built test bench designed and manufactured by MaterialMates Italia has been installed for the spatially resolved characterisation of fuel cells. It consists of 50 synchronised potentiostats as well as 50 channel frequency response analyser (FRA) that enables the simultaneous measurement of cell impedance as well as current and voltage at 50 cell segments in potentiostatic and galvanostatic mode, respectively. EIS can be conducted in a frequency range between 0.1 mHz and 20 kHz that offers the opportunity to analyse all loss mechanisms ranging from mass transport problems in the low frequency range and charge transfer losses in the middle frequency range to losses caused by ionic conduction in membrane and catalyst layers impacting at frequencies above 1 kHz.

To reduce the interaction of adjacent cell segments during EIS, even at frequencies up to 10 kHz, the excitation generating potentiostats are hardware-based synchronised. Each FRA measures and analyses the cell response separately and uses a noise-optimised lock-in amplifier. The calculation method of the impedance can be configured freely between highest accuracy and fastest measurement. In addition to the fundamental mode of cell response higher harmonics can be analysed up to 3rd order. This may offer new possibilities to distinguish more precisely between the influence of the present ionic conduction, electrochemical and transport processes in the diffusion layer, micro porous layer and/or catalyst layer. For setting the voltage or current each segment is connected to a separate potentiostat whereas an overall cell current up to 200 A can be handled.

The characterisation of a HTPEM fuel cell was conducted with commercially available MEA sets with an active area of 25 cm^2. The MEA consists of a phosphoric acid doped PBI membrane mounted in a sub-gasket and between two woven gas diffusion electrodes.

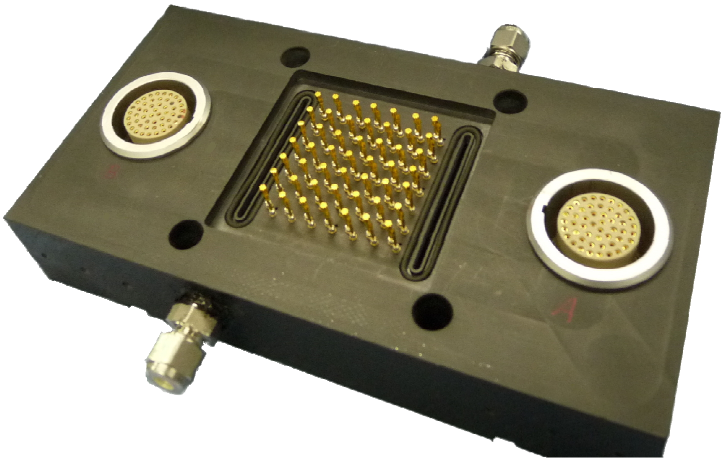

Figure 1: Design of the test cell for characterisation of PEMFCs up to 200°C.

The test cell, shown in Figure 1, is designed and constructed in-house. The key feature is an exchangeable and segmented graphite inlay acting as flowfield which can resist in harsh and acidic environments. Each segment offers an active area of approx. 0.5 cm^2. The design of the segmentation using an exchangeable inlay offers a high flexibility for characterisation of different flowfield geometries in HTPEM fuel cells as well as in conventional PEM fuel cells where the impact of the flowfield design on cell performance and maximum current density is more significant. Electrical contact of the segments is established via gold-coated switch probes for sensing and current collection and further on via two 50 pin connectors. The connection between the test cell and the potentiostats is realised using extremely low-inductive cables. All components dealing with the segmented side are assembled in a polymer block wherein the gas supply is realised.

While segmenting one side of the cell an unsegmented flowfield is assembled at the other side. Temperature distribution of the cell can be measured at selected cell positions in the cathode flowfield. The test cell is mounted in a laboratory oven providing a homogenous temperature distribution outside the test cell to avoid artificial effects caused by varieties in thermal isolation. All assembled components are designed to resist temperatures up to 200 °C.

Gas flow rate is set using digital massflow controller. Since gas humidifiers are assembled the investigation of the relative humidity of the gases on the cell performance is possible up to a dew point of 60 °C. Data acquisition of temperature measurement and gas flow controlling is realised using LabView.

3 Results

Giving an idea of the characterisation method of combined current mapping and electrochemical impedance spectroscopy in a spatially resolved test cell, earlier results of the characterisation of a HTPEM fuel cell are presented in the following. The measurements were conducted at a cell voltage of 0.5 V and at a temperature of 160 °C. During the measurement the stoichiometry of air was varied between $\lambda_{air} = 1.5$ and $\lambda_{air} = 3$, while the hydrogen stoichiometry remained constant at $\lambda_{H2} = 1.3$.

Figures 2 - 4 show the spatial distribution of current density for selected air stoichiometries. The air flow is oriented along the y-axis, while the hydrogen flows along the x-axis into the cell.

For all stoichiometries the current density shows the same characteristics. Along the air flow the current density shows a steep increase from the gas inlets to the 3rd row of segments over a length of approximately 1 cm. Further on towards the gas outlet the current density decreases with a minor gradient. The segment with the maximal current of each row migrates along the hydrogen flow direction leading to a diagonal arrangement of cell segments 9, 17, 25, and 33. The current density at these segments varies between 288 $mAcm^{-2}$ and 240 $mAcm^{-2}$ at segment 17 and segment 33, respectively. The combination of hydrogen and oxygen concentration coupled with the temperature distribution causes the discovered distribution of current density since the maximal current density is located at the optimal ratio between oxygen and hydrogen concentration at the location of the highest temperature.

Reducing the air stoichiometry does not change the characteristics of the current density distribution but as a result the current density decreases towards the outlet of the cathode channels. This phenomenon is caused by a reduced oxygen concentration due to the current generation along the channel. At segment 33 the current density is reduced from 240 $mAcm^{-2}$ at $\lambda_{air} = 3$ to 208 $mAcm^{-2}$ at $\lambda_{air} = 1.5$.

Results of the electrochemical impedance spectroscopy are also shown in Figure 2 – 4 for the cell segments 17, 25, and 33. The excitation frequency was varied between 1 kHz and

100 mHz. At high cathodic air flow of λ_{air} = 3 the Nyquist plot of segment 17 near to the gas inlets shows a nearly semicircular RC member-like behaviour. A second arc cannot be seen at the mentioned operating conditions at that cell segment. The shape of the spectra is different for segments 25 and 33 since at both segments a second arc appears at frequencies of several Hz. This indicates a higher mass transfer resistance due to a worse or rather slower gas feed than near the air inlet.

Reducing the air flow leads to significant changes in impedance spectra since both the first and the second arc grow in diameter for all analysed segments. Especially at a cathode stoichiometry of λ_{air} = 1.5 the second arc of the latter segments is remarkably more pronounced which is caused by a stronger diffusion polarisation at lower oxygen concentrations. These results are in agreement with the investigations of Jespersen et. al. who carried out electrochemical impedance spectroscopy in HTPEM fuel cells [6].

The high frequency resistance (HFR) at 1 kHz is approx. 160 mΩcm^2 and does not vary with position and operating conditions at the selected cell segments.

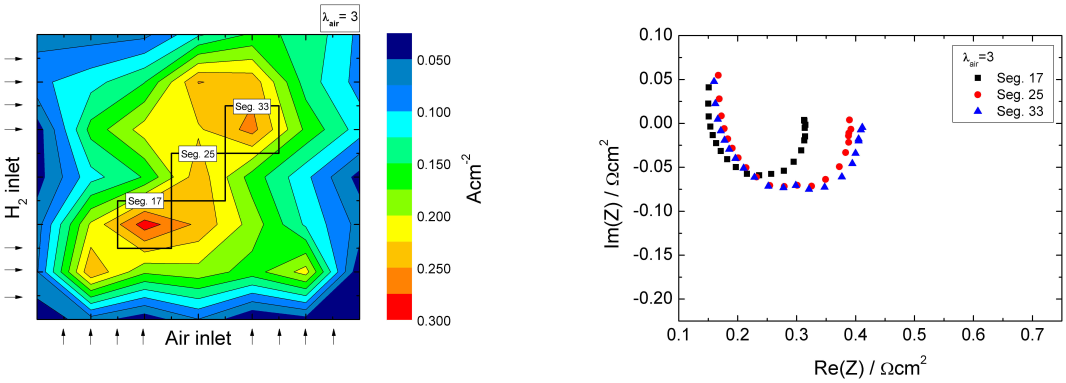

Figure 2: **Current density distribution (left) and Nyquist (right) plot of EIS at selected cell segments for a cathode stoichiometry of λ_{air} = 3.**

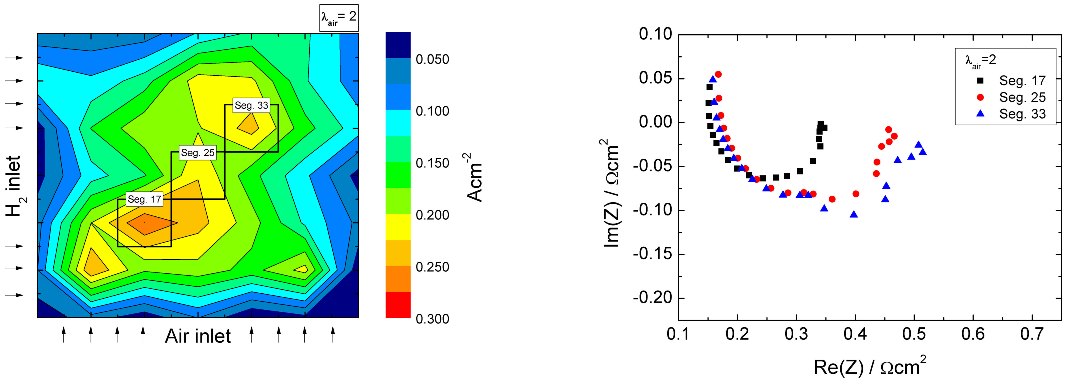

Figure 3: **Current density distribution (left) and Nyquist plot (right) of EIS at selected cell segments for a cathode stoichiometry of λ_{air} = 2.**

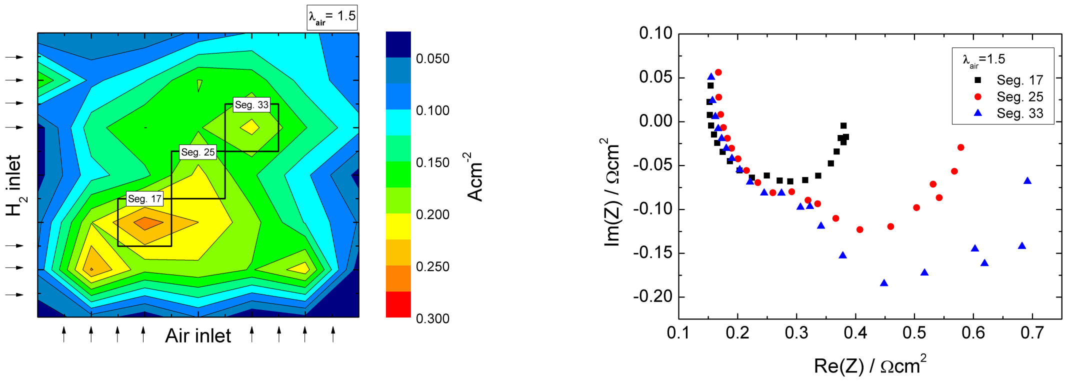

Figure 4: **Current density distribution (left) and Nyquist plot (right) of EIS at selected cell segments for a cathode stoichiometry of $\lambda_{air} = 1.5$.**

4 Conclusion

In this work, a newly developed, unique 50-channel potentiostat-impedance spectrometer and an in-house designed and manufactured test cell is described in detail. This test facility enables the spatially resolved characterisation of polymer electrolyte membrane fuel cells at temperatures up to 200 °C. Thus, lateral inhomogeneities caused by mass transport losses, membrane dehydration, and catalyst poisoning effects can be investigated at different operating conditions. A sophisticated in-house designed test cell including an exchangeable and segmented flowfield is presented. The cell offers a great flexibility for investigating the influence of different flowfield designs on the conventional as well as high temperature PEM fuel cells.

As an idea of example characterisations which can be conducted with the test bench, the influence of cathodic gas stoichiometry on the spatial distribution of the present processes in a HTPEM fuel cell has been investigated using current density measurements as well as electrochemical impedance spectroscopy. It has been shown that reducing the air flow leads to changes in the spatial distribution of current density and the impedance spectra. More precisely a stronger gradient along the cathodic gas channel appears as well as the Nyquist plot shows more pronounced second arcs at cell segments towards the air outlet. The characteristics of impedance spectra are highly dependent on the position. The HFR does not depend on cathode stoichiometry and does not vary between the investigated segments.

With the presented results it can be concluded that measuring the overall cell impedance might not lead to a complete picture of the processes that determines the fuel cell performance since the impact of lateral inhomogeneities merges the cell response to a non-interpretable spectra. Thus, spatially resolved electrochemical impedance spectroscopy is necessary to achieve a deeper understanding of the present processes in a fuel cell.

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