Fast Locally Resolved Electrochemical Impedance Spectroscopy in Polymer Electrolyte Fuel Cells

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Electrochemical impedance spectroscopy (EIS) is a powerful tool for *in situ* diagnosis in polymer electrolyte fuel cells (PEFC) [1]. Limiting processes, e.g. diffusion, charge transfer or ohmic resistance, can be assessed under different operating conditions. By using this method in a segmented cell locally resolved EIS measurements are possible and limiting processes affecting the lateral current distribution can be identified.

While other setups proposed for locally resolved EIS in PEFCs [2,3] are suffering from long recording times, with our setup described here the recording time for a locally resolved EIS spectrum is comparable to the time required to obtain an integral EIS spectrum, and it is virtually independent on the number of segments use in a segmented PEFC. Furthermore, instead of using idealized cells [3], we are using a realistic PEFC operated on pure H_2/O_2 (Fig. 1) with a nine-fold segmented serpentine cathode flow-field and an unsegmented serpentine anode flow-field (area 29,2 cm^2). The cell is operated in galvanostatic mode. The impedance measurement is performed for all 9 segments in parallel by a multichannel EIS measuring system developed in our laboratory.
This device is able to handle cell currents of up to 60A and modulation frequencies up to 10kHz. The impedance of each segment and furthermore the current distribution is calculated for each modulation frequency applied.

The results for co-flow of the reactant gases are shown in Fig. 1-3. The benefit of an increasing relative humidity along the gas channels due to the formation of product water is clearly demonstrated (Fig. 1). As the current density increases from the gas inlet to the outlet, the modulus of the impedance $|Z|$ decreases in principle for all modulation frequencies (Fig. 2). The small drift and variation of $|Z|$ for seg. 1-3 is due to the very low humidity at the gas inlet and the low current density of these segments. This drift is accompanied by a drift and variation in current density of these segments. Segments 6-9 have the highest current densities (@I_{cell}=16A). The modulus and phase of the impedance of these segments (Fig. 2) show comparable characteristics. However, the slightly increasing current density to the outlet is reflected in a decreasing ohmic and charge transfer resistance R_{CT} (Fig. 3) due to increasing relative humidity, whereas seg. 8 and 9 have comparable values for R_{CT}. Segments 1-3 have by far the worst performance (@I_{cell}=16A). The slightly decreasing current density towards the inlet is accompanied by a strong increase in the modulus of the impedance and thus R_{CT} (Fig. 2). Furthermore, unlike for segments 6-9, an increasing phase shift φ to higher frequencies occurs, resulting in an additional high frequency arc in the Nyquist plot (not shown here). Since the phase shift φ increases from seg. 3 to 1 and thus increases with decreasing current density and humidity this might be due to insufficent water in the membrane [4] or in the granular electrode structure and thus increasing contact capacitance and distributed ohmic resistance [5]. This is corroborated by the fact that these segments also have the highest charge transfer resistances due to loss of electrochemically active surface with decreasing ionic conductivity in the catalyst layer. Thus the performance loss of seg. 1-3 can be mainly attributed to drying of the catalyst layer, whereas seg. 6-9 are well humidified, since no increasing value of φ is observed at higher frequencies for these segments, while seg. 4-5 show values in between.
Further details of the measurement system and its application to the investigation of the influence of various parameters, e.g. humidity, co/counter flow, current density or temperature on the performance of a H_2/O_2-PEFC will be discussed in the presentation.

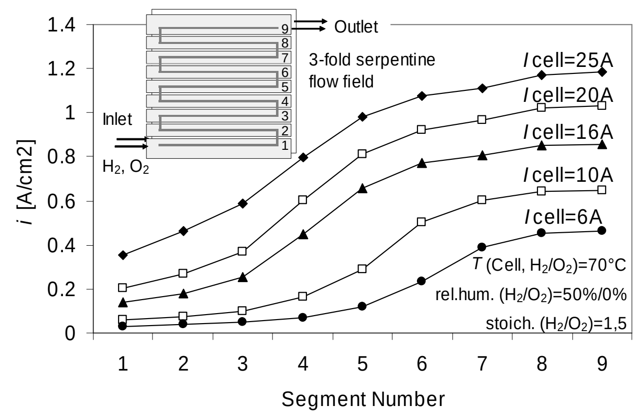

Fig. 1: Segmented PEFC and dc current distribution at different cell currents I_{cell} (Nafion 115 membrane, Pt-black electrodes 4,2mg Pt/cm^2)

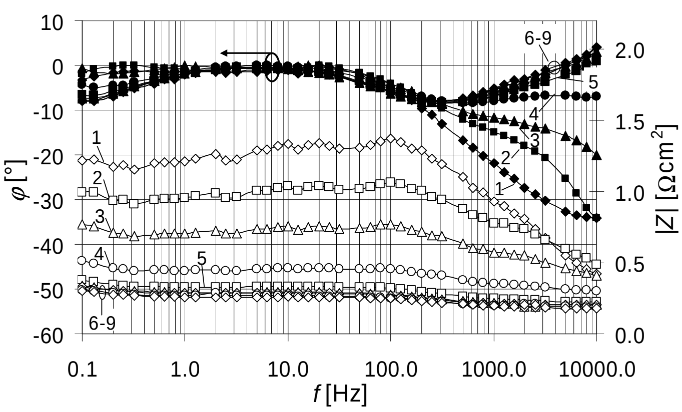

Fig. 2: Locally resolved EIS spectrum of segments 1-9 @ I_{cell}=16A

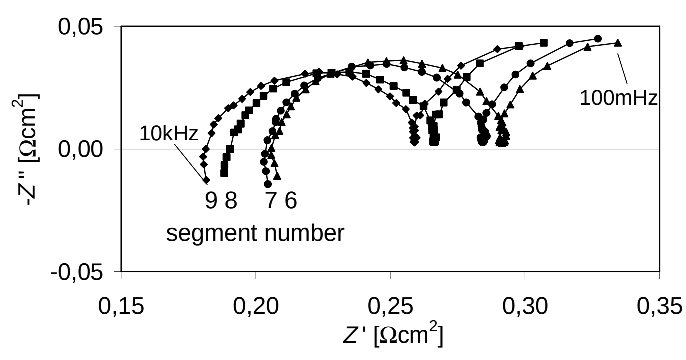

Fig. 3: Nyquist plot of segments 6-9 @ I_{cell}=16A

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