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Relation of Local Cell Voltage and Current Density Distribution during Fuel Starvation in PEMFC Stacks

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Abstract

Gross fuel starvation is a harmful degradation stressor to polymer electrolyte membrane fuel cell (PEMFC) stacks. However, it is extremely difficult to fully avoid these events for integration level of fuel cell system and vehicle. In stack setups, properly reactant-supplied cells can apply their voltage to an undersupplied cell due to their electric serial connection. This can cause drastic local negative cell voltages, leading to substitutional reactions like the harmful carbon oxidation reaction.
The presented study uses a 3-cell stack to illustrate how properly media supplied cells can apply their cell voltages to a starved cell. This stack consists of state-of-the-art automotive-sized membrane electrode assemblies and carbon composite bipolar plates. Fuel starvation of one cell was generated by an additional flow resistance in the hydrogen media inlet port. The local current density distribution of the starved cell showed two distinct regimes. These regimes suppose the occurrence of different electrochemical reactions along the flow direction. The progression of each fuel cells voltage along the flow field were measured by cell voltage monitoring measurements at eight positions. The voltage of the starved cell was found to be strongly inequal over the flow direction with intense negative voltages towards the fuel outlet. The occurrence of this non-equal cell voltages was explained by local measurements of the flow field plate potentials.
A mechanism is proposed, which results in an increased carbon oxidation of the anode catalyst layer towards the fuel outlet during fuel starvation. This mechanism is unique to multi-cell fuel cells because it is based on the mutual distortion of cell voltages caused by electric interaction of adjacent fuel cells during gross fuel starvation.

Introduction

Low temperature polymer electrolyte membrane fuel cells (PEMFC) are a promising technology to reduce local greenhouse gas emission of the mobility and transportation sector. One important key-enabler to improve their large-scale industrial applicability is understanding and reduction of PEMFC performance degradation.
Gross fuel starvation of single cells in a multi-cell stack is an error state, which is known to cause intense irreversible degradation. Several mitigation strategies were developed to circumvent this degradation stressor. Hardware and software mitigation strategies are typically implemented to fuel cell systems of large-scale multi-cell stacks. However, despite these efforts, the occurrence of fuel starvation cannot fully be excluded over several thousands to ten thousand of operation hours. Consequently, electrochemical co-catalysts are often added to the anode catalyst layer as an additional mitigation strategy. The reaction rate of the harmful carbon oxidation reaction of the anode carbon support during fuel starvation is therefore reduced by the alternative oxygen evolution reaction. This mitigation strategy does not fully suppress the degradation during fuel starvation. Instead, it drastically increases the time until the fuel cell creases to function.
Testing the reversal tolerance of PEMFC membrane electrode assemblies (MEA) is typically performed on laboratory-scale single cells. In these tests, a negative voltage is applied via an external power source. This negative voltage imitates the error case of a fuel starved cell in a serial connection with other healthy, non-starved fuel cells in a stack assembly. How this lab-scaled testing translates to multi-cell stacks of large geometry is still a not well investigated question in today's fuel cell research.

1. Scientific Approach

The presented study proposes an approach to artificially generate fuel starvation on a multi-cell stack. This approach is applied to a 3-cell stack assembly of automotive-sized MEAs. The resulting current density distribution of the starved cell is investigated. Simultaneously, the interaction between the fuel starved cell with the two non-starved healthy cells is investigated by an 8-fold multipoint cell voltage monitoring approach.
The results underline, that scale-up phenomena between these integration levels greatly complicate the knowledge transfer of gross fuel starvation mitigation strategies.

2. Experimental

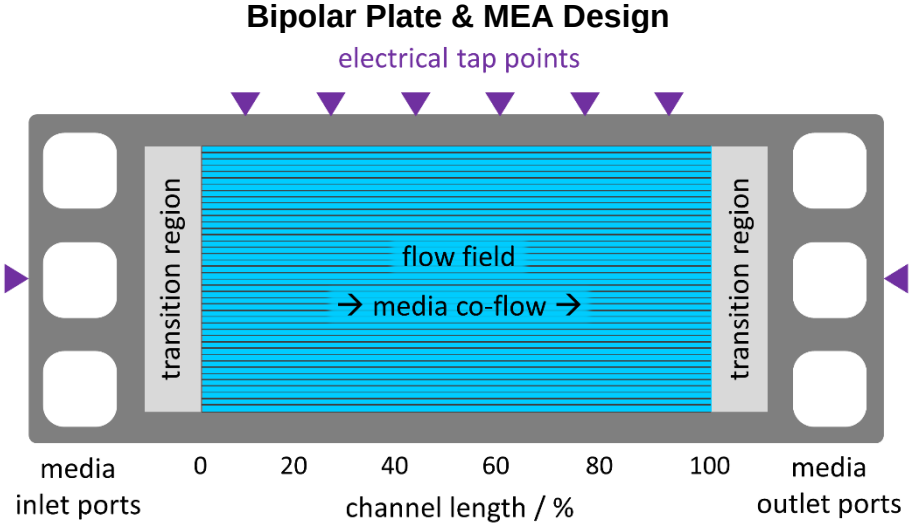

Figure 1: Geometry of the bipolar plate and positioning of the electrical tap points.

Figure 1 shows the design of the carbon composite flow field plates and the positioning of the electric tap points. The design contains media ports for all three media (air, fuel, coolant), which are connected by transition regions to the central straight-channel flow field. All media pass the stack in co-flow. Nitrogen diluted hydrogen was used as fuel. The bipolar plates (BP) contained flow fields for all three media, but interface plates (IP) lack the outer reactant flow field.
The membrane electrode assembly consists of a polytetrafluorethylene reinforced ionomer membrane and catalyst layers with carbon supported pure platinum catalyst, sandwiched between paper-like gas diffusion layers. The anode catalyst layer furthermore contains a cell reversal tolerant co-catalyst (e.g., IrO2) to promote the reaction rate of the oxygen evolution reaction (OER) during cell reversal.

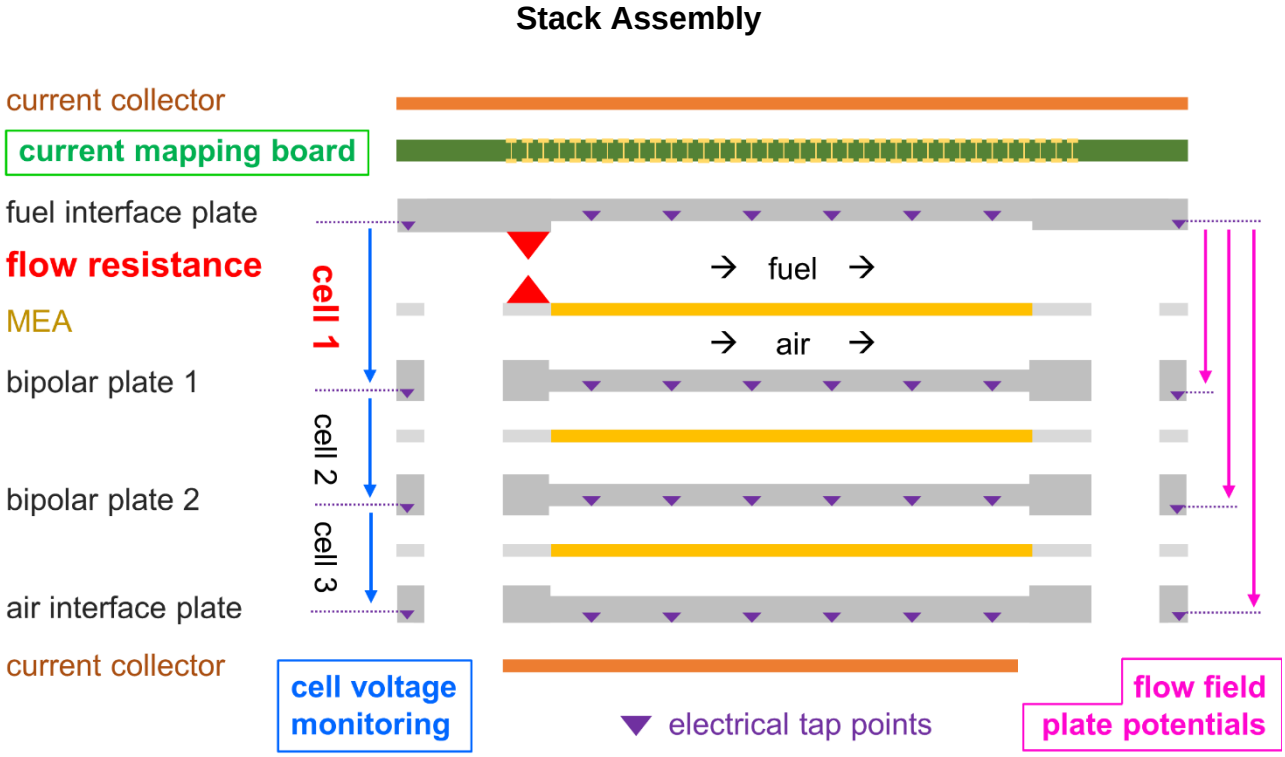

Figure 2: Schematic drawing of the 3-cell PEMFC stack assembly. Utilized measurement techniques are marked with a box. The flow resistance to generate intentional fuel starvation of cell #1 is depicted in red.

Figure 2 depicts the experimental setup of the 3-cell stack assembly, which is sandwiched between highly electrically conductive current collector plates. Furthermore, the additional measurement techniques of current density distribution, cell voltage monitoring, and flow field plate potentials are depicted.
Fuel starvation of cell #1 was modeled by increasing its flow resistance for the fuel media flow. This was done by adding a 60µm thick KAPTON foil between the frame of the MEA of cell #1 and the fuel interface plate. In this foil, pinholes were added by a thin needle. The flow resistance of the fuel reactant flow was therefore increased. Cell #1 is consequently supplied with a reduced amount of hydrogen, compared to the other cells. By this technique, a fuel starvation was modelled. Because the cell reversal tolerant catalyst can largely mitigate the COR for a prolonged time frame, a quasi-steady-state operation was achieved. During a time of about one minute, all presented electric measurements of the stack were performed.

The current density distribution was inspected by a current mapping board, manufactured by S++ SIMULATION SERVICES. This custom-produced printed circuit board resolves the local current density by an array of 36 sensors in flow direction and 18 sensors across flow direction. The inner 30 times 14 sensors span the electrochemically active area, the other sensors are located beyond. The current density of the starved cell #1 was inspected by the chosen positioning of the board between the fuel IP and the current collector plate, as depicted in figure 1.
The electrical tap points were used to perform cell voltage monitoring (CVM) and flow field plate potential measurements by a ZAHNER IM6 potentiostat, see figure 1 and figure 2.
For a CVM measurement, the voltage between two neighboring flow field plates is measured for all cells. A multipoint CVM measurement records this CVM at typically two measurement points. In the present study, this concept was extended to eight tap points. This way, the spatially resolved cell voltages along the flow direction were recorded.
In the flow field plate potential measurement, voltages between a fixed reference point and each tap point of each flow field plate were recorded. As reference potential, the electrical tap point of the fuel interface plate at the outlet was selected.

3. Results & Discussion

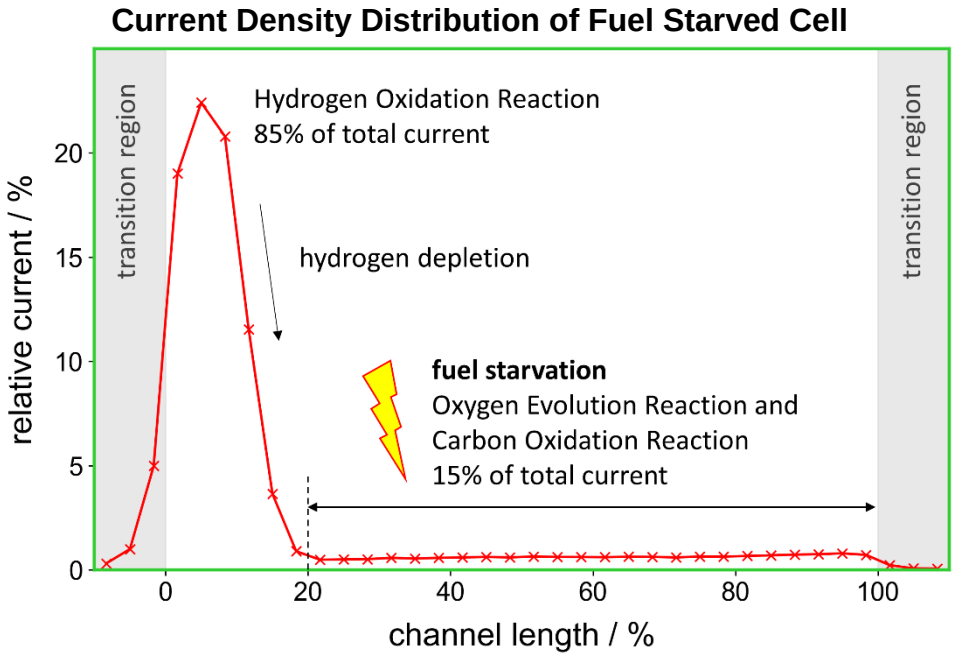

Figure 3: Current density distribution along flow direction of fuel starved cell #1 in a 3-cell stack assembly.

Figure 3 shows the current density distribution of cell #1 in the 3-cell stack assembly along the flow direction. The flow resistance at the hydrogen inlet of cell #1 was artificially increased by the described method. Besides this modification, the overall stack operation was in a typical range for this kind of automotive MEA and a stack current was selected, which represents an intermediary power range.
The current density distribution profile of fuel starved cell #1 shows two distinct regimes. These regimes are sharply separated and are assigned to regions of different electrochemical reactions:

- In the first 20% of the active area in flow direction, a very high current density is obtained. The decrease of mass flow of reactants is known to cause a current density redistribution towards the inlet of this reactant flow under galvanostatic conditions [1].

This current redistribution occurs due to an increased drop of reactant partial pressure and therefore an increased overpotential along the flow channels.
For a decrease of oxygen mass flow, this phenomenon is already visible at comparatively high stoichiometries due to the sluggish oxygen reduction reaction. For a reduction of hydrogen mass flow, this redistribution phenomenon rather starts to appear at stoichiometries close to 1, because the hydrogen oxidation reaction is accompanied by much lower overpotentials [1].
This high current density regime at the inlet is consequently mainly attributed to the HOR, which is the normal anode reaction in fuel cells.

- Over the latter 80% of the active area in flow direction, another regime of current density is observed. The current density in this region is much lower and attains an almost flat shape. The total current in this regime accounts for 15% of the stacks total current. This current is assigned to the substitutional reactions during fuel starvation, namely the OER and COR.

A fuel stoichiometry of 0.85 was calculated for the fuel starved cell #1, based on these current regimes. This current density profile suggests, that the harmful OER reaction only occurs within the latter regime. This suspect is further inspected by local cell voltage monitoring measurements in the following.

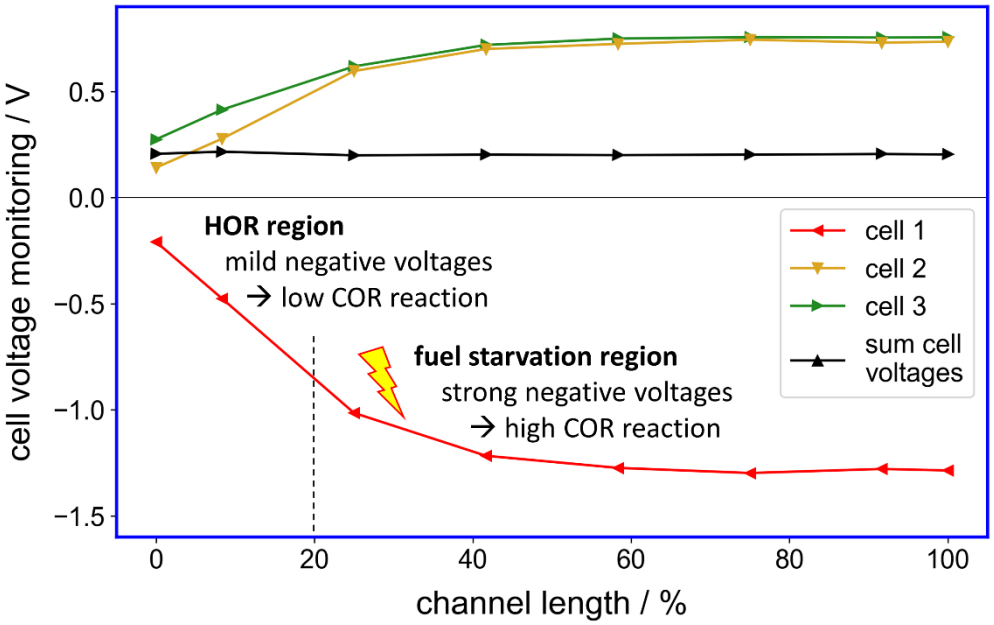

Figure 4: Multipoint cell voltage monitoring along the flow direction during fuel starvation of cell #1 in a 3-cell stack. The black dashed line represents the separation of hydrogen oxidation reaction (HOR) region and fuel starvation region from the current density distribution measurements in figure 3.

Figure 4 shows the local cell voltage of all three cells along the flow direction. The local voltage of the fuel starved cell #1 strongly decreases in flow direction. Voltages below -1V are observed in the latter 80% in flow direction, which was identified as the region of fuel starvation by the current density distribution measurements. The carbon oxidation reaction is known to increase in its reaction rate by more negative cell voltages [2]. At such intense negative local cell voltages, the substitutional reactions of OER and COR are therefore expected in this region. Due to the progression of local voltage of cell #1, a more pronounced degradation by carbon oxidation is consequently expected in this starvation region, compared to the HOR region.

The non-starved cells #2 and #3 increase in cell voltage along the flow direction. In total, the sum of all three voltages is equal to the stack voltage of 0.2V at each measurement position. To better explain the phenomenon of inequal cell voltages along the flow direction, the flow field plate potentials are inspected in the following.

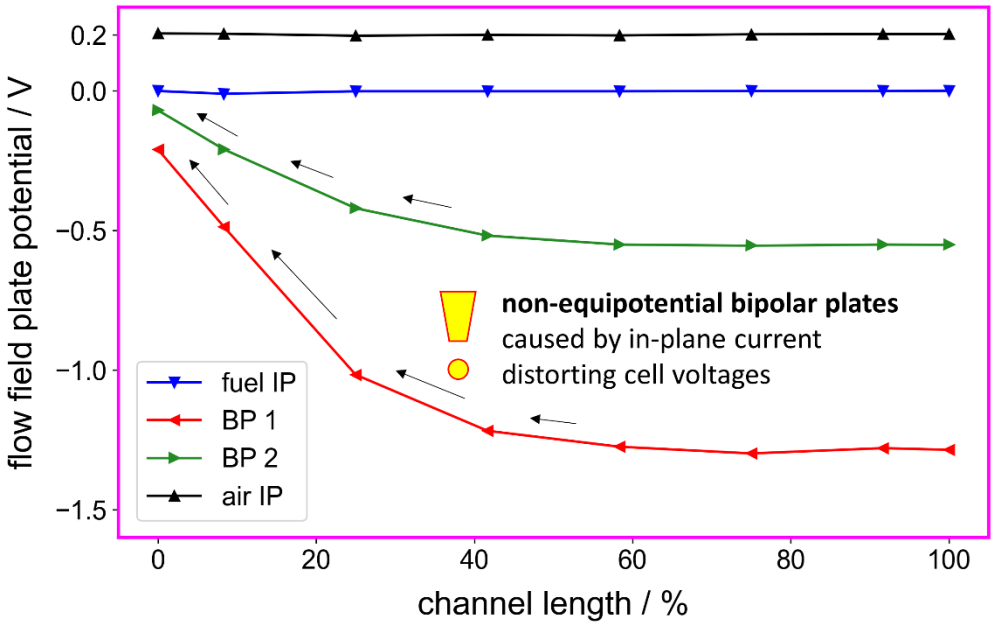

Figure 5: Flow field plate potential measurements along the flow direction during fuel starvation of cell #1 in a 3-cell stack. The potential of the fuel interface plate at the media outlet position was used as electrical reference point.

Figure 5 shows the measurement of flow field plate potentials during the fuel starvation of cell #1. In this graphical representation, cell voltages are equal to the differences between adjacent flow field plates. For example, local voltage of the fuel starved cell #1 is equal to the potential difference of the fuel IP and the BP #1. The potential difference between fuel IP and air IP is equal to 0.2V for all tap points, which is equal to the stack voltage. It becomes visible, how the non-starved cells #2 and #3 imprint a large part of their positive voltage to the fuel starved cell #1, resulting in a reversal of the cell polarity. This imprinted negative voltage acts as a power source to enable the parasitic reactions during fuel starvation.
Both BPs show intense local potential gradients in the former half of the active area. These potential gradients in in-plane direction of the conductive BPs are co-occurring with electrical currents, according to Ohm's law [3]. At the same time, this gradients in BP potentials result in the observed distortion of the local voltages for all three cells.

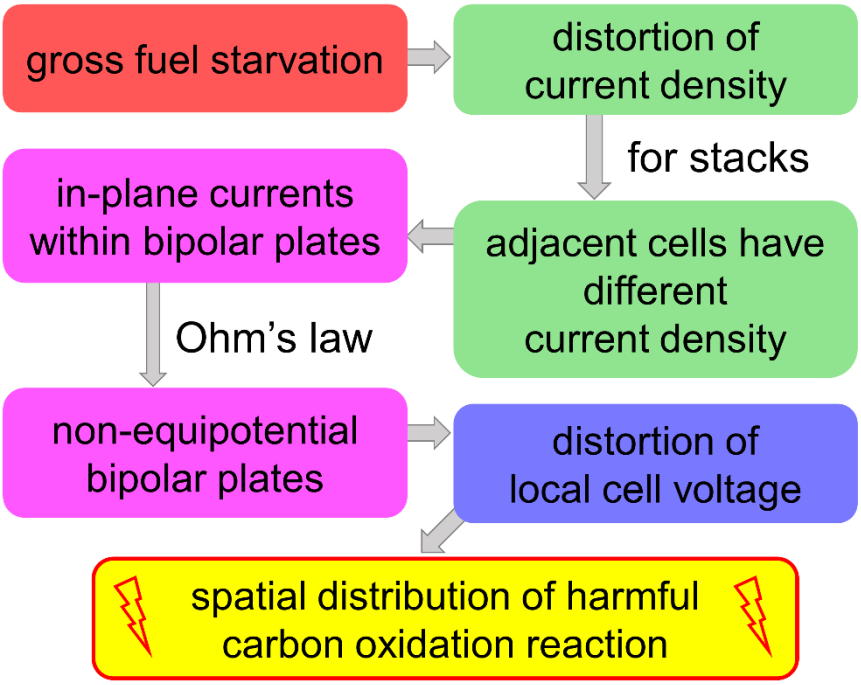

Figure 6: Proposed mechanism, which suggests a spatial distribution of the harmful carbon oxidation reaction under fuel starvation for stacks of large-sized low-conductive bipolar plates.

Figure 6 proposes a mechanism, by which the effect of fuel starvation on automotive PEMFC stacks differs from laboratory single cell operation. This mechanism combines the previously discussed results of spatially resolved current density, flow field plate potential and cell voltage monitoring measurements.

Cells of a PEMFC stack typically share their reactant media in a parallel-connection. Due to this flow-sharing, an inequal distribution of reactant over the cells can occur, if cells have non-equal flow resistances. In extreme cases, one cell in a stack may be supplied by a too low amount of reactant for the drawn current, called gross starvation.
The stoichiometry of reactant is known to influence the current density of fuel cells. Especially gross reactant starvation under galvanostatic conditions leads to a strong distortion of current density. The resulting current density profile shows a very high current density in the inlet region and a much lower current towards the outlet. This current redistribution is observed for fuel cells in single cell and stack assembly. The starvation of an individual cell in a stack leads to differences of current density profiles of adjacent cells. These inequal profiles demand for in-plane currents within their sandwiched BP. Such in-plane currents are accompanied by in-plane potential gradients, according to Ohm's law.
Simultaneously, the local voltage of a fuel cell is equal to the local potential difference of its embracing flow field plates. Therefore, the observed non-equal BP potentials distort the cell voltage of the fuel cells.
A fuel starved cell in a stack can be pushed to a reversal of its cell voltage by other non-starved cells. This externally applied voltage can greatly vary over the active area, following the proposed mechanism. The reaction rate of the harmful COR is known to increase by more negative cell voltages during reversal. Therefore, the observed separation of current density regimes and cell voltage progressions suggest a higher degradation by the harmful COR in the marked starvation region.

4. Conclusions

The reaction of a 3-cell stack for fuel gross starvation of one individual cell was presented. Non-equal voltages over the MEA of the starved cell were found. Therefore, an inequal distribution of the harmful carbon oxidation reaction is suspected. A mechanism for this inequal voltage distribution was proposed.

In combination of current density and CVM measurements, two different MEA regions were separated. It is expected, that in this regions, different reactions occur. It was therefore possible to determine the stoichiometry of a fuel starved cell with a high-resolution current mapping board.

The positioning of an electric tap point is relevant to detect the error state of gross fuel starvation. This is especially true for carbon composite bipolar plates because they typically have much lower in-plane conductivity than metal bipolar plates. The usage of a multipoint CVM is therefore highly recommended for stacks, which use carbon composite bipolar plates [4].

References

[1] A. Manokaran and S. Pushpavanam and P. Sridhar, Dynamics of anode–cathode interaction in a polymer electrolyte fuel cell revealed by simultaneous current and potential distribution measurements under local reactant-starvation conditions. Journal of Applied Electrochemistry, 2015, DOI: 10.1007/s10800-015-0800-9.

[2] R. Marić and C. Gebauer and M. Nesselberger and F. Hasché and P. Strasser, Towards a Harmonized Accelerated Stress Test Protocol for Fuel Starvation Induced Cell Reversal Events in PEM Fuel Cells: The Effect of Pulse Duration. Journal of The Electrochemical Society, 2020, DOI: 10.1149/1945-7111/abad68.

[3] M. Le Ny and O. Chadebec and G. Cauffet and J. M. Dedulle and Y. Bultel, A Three Dimensional Electrical Model of PEMFC Stack. Fuel Cells, 2012, DOI: 10.1002/fuce.201100101.

[4] Z. Hu and L. Xu and J. Li and J. Hu and X. Xu and X. Du and W. Sun and M. Ouyang, A cell interaction phenomenon in a multi-cell stack under one cell suffering fuel starvation. Energy Conversion and Management, 2018, DOI: 10.1016/j.enconman.2018.08.062.

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