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Short communication

Simultaneous electrochemical impedance spectroscopy of single cells in a PEM fuel cell stack

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Abstract

A measurement set-up is presented containing a multichannel frequency response analyser system that allows the measurements of impedance spectra of single cells in a fuel cell stack simultaneously.

As a proof of reliability, the sum of the impedances of the single cells is compared to the measured impedance of the whole stack. A good correlation was found. The absolute deviation is less than 2.5%.

A measurement of the stack during low load operation is presented. Differences in the individual cell voltages are investigated. A flooding event in a single cell is observed by means of the impedance measurement minutes before the polarisation shows a voltage drop.

Keywords: PEM; Fuel cell; Stack; Impedance; EIS

1. Introduction

In PEM fuel cells, the membrane needs a sufficient water content for good proton conductivity [1]. On the other hand, condensed water in the porous media or the gas channels can cause gas transport limitations. Therefore, passive water management in portable and micro fuel cells is an important issue, as gas humidifiers and active cell cooling usually cannot be used.

The measured impedance spectrum can help to explain the performance of a cell. It offers by far more information about the condition of the cell than a simple current/voltage measurement. In particular, membrane conductivity, activation and mass transport limitations can be observed more explicitly. Using a current interrupt method, ohmic losses due to poor proton conductivity of the membrane can be measured [2]. This is not sufficient as measuring diffusion losses is essential for characterising and controlling a PEM fuel cell [3].

Since integral measurements of the whole stack do not obtain information about single cells, only the simultaneous impedance spectroscopy of the single cells in a stack is capable of evaluating the state of operation of the single cells at the same time and therewith explaining overall stack performance.

2. Experimental

A self-developed short stack consisting of four cells with an active area of 53 cm^2 each is used.

The cathode gas is humidified in a bubbler. The humidified gas is mixed with dry gas to set the desired dew point temperature. The dew points of the anode and cathode gas streams are measured using dew point mirrors. The measurements presented here were taken at dew point temperatures of −20 °C for the anode gas and 14 °C for the cathode gas. The gases were provided to the cell at room temperature. The stack outlets are open to ambient. Stack temperature was not measured.

A data logging system measures the DC voltages of the single cells.

A Solartron 1254 Frequency Response Analyser (FRA) with two 1251 multichannel extensions is available for impedance measurement of up to 19 single cells of a PEM stack. A Kepco BOP 20/20 bipolar power supply was used as load. It is operated in current control mode with the ac perturbation above a dc bias analog programmed by the generator output of the 1254 FRA.

The current is applied to the whole stack. The perturbation of the current is measured at a 100 mΩ shunt resistor connected in series with the cell, whereas the voltage perturbations are measured for every single cell with an individual input of the FRA.

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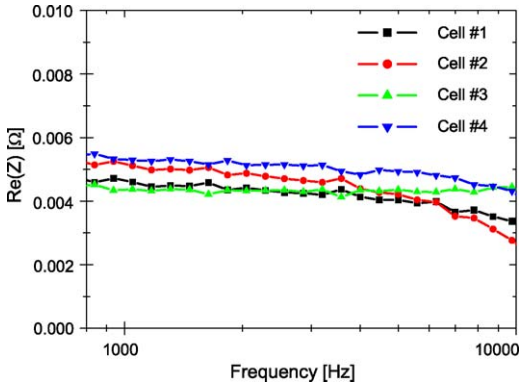

Fig. 1. Typical measurement of the real part of the impedance in the high-frequency range.

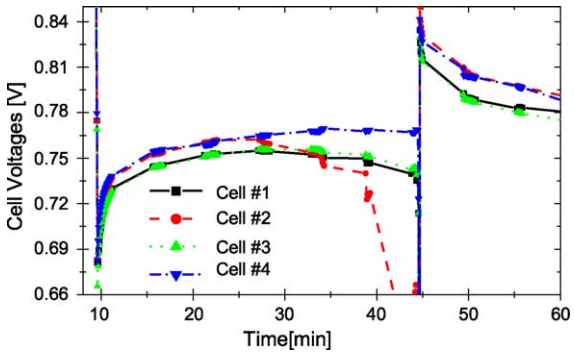

Fig. 2. The voltages of the individual cells.

For measuring the impedance spectra, 40 points are taken in a frequency range from 100 mHz to 10 kHz. For an excitation in voltage less than 10 mV amplitude the response of the fuel cell is assumed to be linear [4]. The chosen amplitude of 250 mA for the current excitation is small enough for measuring impedances up to 0.04 Ω.

Additionally, to validate the measurement set-up the voltage perturbation of the whole stack was measured. This was compared to the sum of the single cell voltage perturbations.

In all cases and all frequencies, the deviation between single cell voltages and the sum of the single cell voltages is smaller than 2.5%. Therefore, the measurement set-up is assumed to be sufficiently accurate to measure single cell impedances.

The membrane resistance together with the backing, bipolar plate, and contact resistances is given by the real part of the high-frequency end of the charge transfer arc [3,4]. Fig. 1 shows the real part of a typical impedance measurement. As can be seen, there are only minor changes in the value of the real part between 1 and 10 kHz. Therefore, the real part of the impedance at 1 kHz is used as an estimation. This estimation is termed high-frequency resistance R_{hf}. It provides good evidence about change in proton conductivity of the membrane due to water content and relative deviations in resistances of the individual cells due to differences in fabrication.

3. Results and discussion

The stack was operated with a current of 4 A. This is a low load point for a fuel cell stack of this size. But this power could be the demand for a system for several hours with the consumer load is in standby mode.

The voltages of the individual cells are shown in Fig. 2. The load is switched on 9.5 min after applying the reactant gases. The gas flow rates are set to 300 ml min^{-1} dry hydrogen for the anode and 1000 ml min^{-1} for the cathode. Impedance spectra are taken approximately every 7 min. The duration of the measurement of one spectrum is (4.5 min. During the impedance measurements the cell voltages are not monitored.

After the load is switched on cell voltages drop to around 670 mV. Due to an initial decay of the electrochemical losses, cell voltages rise over the first period of operation. The voltages of the cells 1 and 3 are about 10 mV below cells 2 and 4. The first impedance spectra taken 12 min after the start of the experiment are shown in Fig. 3-M0. All four spectra are similar in shape. There are no significant deviations in the high-frequency resistance. Cells 1 and 3 show larger charge transfer arcs causing slightly lower cell voltages. This explains lower performance of these two cells by lower electrochemical activity. The emergence of a second arc in the frequency range below 1 Hz suggests minor mass transfer losses [3,5,6].

To investigate this situation more thoroughly a second measurement was performed later, showing the same initial situation. The airflow rate was then doubled to 2 l min^{-1}. The effects of the change in the airflow rate on the impedance spectra is presented in Fig. 4. The corresponding cell voltages are shown in Table 1. The change of cell voltages measured before and after this impedance measurement is below 3 mV. By doubling the airflow rate to 2 l min^{-1}, the low-frequency arc vanishes. This can be explained with a change in the stoichiometry coefficient and a lower liquid water content in the porous media as more water is transported out of the cell with the air stream. There are only minor changes in the real part of the low-frequency end of the spectrum. There is no significant performance loss due to operating the cell with an airflow rate of only 1 min^{-1}. The change in cell voltages due to the higher airflow rate is negligible. Since differences in the individual cell voltages do not vanish with a higher airflow rate, these voltage differences are not attributed to improper air distribution in the stack.

The impedance measurement after 30 min is shown in Fig. 3. Fig. 3-M3 shows an increase of the low-frequency arc in the spectrum of cell 2. This indicates an increase in diffusive losses. The cell voltage decreases to the level of cells 1 and 3.

In the next measurement, Fig. 3-M4, the spectrum of cell 2 shows an almost linear 45° branch in the low-frequency

Table 1
The cell voltages at two different airflow rates

Cell number	1 l min^{-1} (mV)	2 l min^{-1} (mV)
Cell 1	752	755
Cell 2	763	765
Cell 3	751	754
Cell 4	768	771

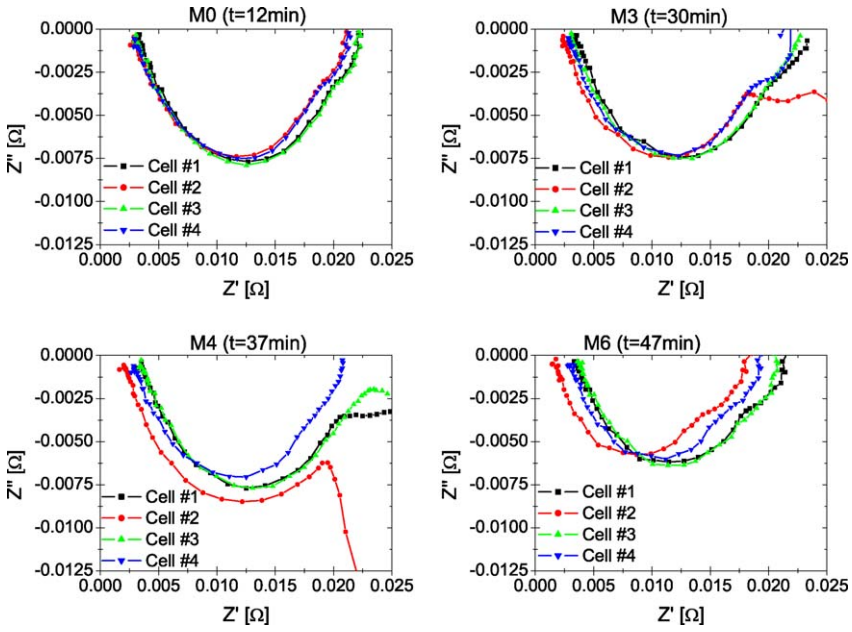

Fig. 3. The impedance spectra measured at different times after the start of experiment.

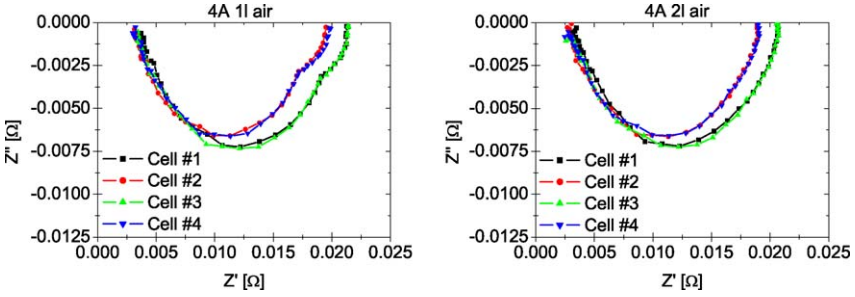

Fig. 4. The impedance spectra at different airflow rates. Left: 1 l min^{-1}, right: 2 l min^{-1}.

range, which depicts a Warburg diffusion behavior. This is a sign for a severe diffusion loss that causes a further decrease in cell voltage. Furthermore, a lower high-frequency resistance indicates a better membrane hydration, and a larger charge transfer arc can be explained by the partial flooding of the active catalyst surface. The spectra of cells 1 and 3 now show a rising low-frequency arc, too. Therefore, cell 4 is the only one in which voltage is not decreasing.

Now the stack faces a diffusion problem most severe in cell 2. This problem is most likely due to product water covering active catalyst surface, which fills the pores and blocks gas channels. The voltage of this cell drops dramatically 9 min after the first evidence in the impedance spectrum as in Fig. 2 (39 min). To overcome this performance loss, the cathode outlet of the stack is closed momentarily to apply a pressure release impulse to the cathodic gas stream. This removes the liquid water off the gas channels.

The cell voltages jump to higher values as before after a short breakdown during the pressure release impulse as shown in Fig. 2 (44 min).

In Fig. 3-M6, the impedance spectra return to the shape they had at the beginning of the measurement. The charge transfer arcs are slightly smaller and the spectrum of cell 2 has shifted towards the lower real parts, which is explained by a better hydration of the membrane after the flooding event.

Looking at the high-frequency resistance in Fig. 5, cell 1 initially has a slightly higher high-frequency resistance, which could be explained by a higher contact resistivity due to deviations in the fabrication process. However, there is no significant impact on the cell voltage. For the first three measurements, the

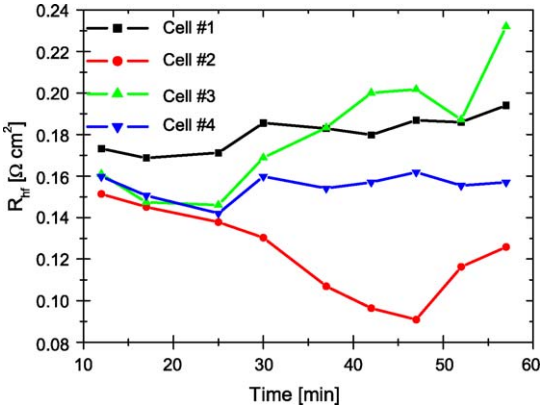

Fig. 5. Progression of the high-frequency resistances.

high-frequency resistances show a slight decline due to membrane wetting with product water. For the measurement at 30 min this effect continues only for cell 2 whereas the resistance rises in the other cells. The parallel gas streams in the stack is one possible explanation. A complete blocking of the gas channels of cell 2 with water would increase the gas flow rates in the other cells, drying them. The pressure release impulse applied at a runtime of 44 min opens up the gas channels of cell 2 again and a dehydration of the membrane sets in 3 min later, rising the high-frequency resistance of cell 2 and lowering those of the other cells. The effect of drying and wetting is strongest in cell 3.

The influence of these changes in high-frequency resistance on cell voltage is small. A change in resistance of $0.1\,\Omega\,cm^2$ leads to a voltage drop of only around 8 mV.

4. Conclusion

A measurement set-up is presented which allows the measurement of impedance spectra of the single cells within a fuel cell stack simultaneously. The sum of the impedances of the single cells is compared to the measured impedance of the whole stack with a resulting deviation of less than 2.5%. The measurement of the stack during partial load operation shows differences in the individual cell voltages. A deficit in the air manifold of the stack can be excluded. A flooding event in a single cell is observed with the impedance measurement minutes before it shows up as a voltage drop.

The simultaneous impedance measurement of the individual fuel cells in a stack offers a more detailed insight into the fuel cell performance than is possible with a DC single cell voltage observation. Even measuring the membrane resistance is not sufficient since these losses have only a minor impact on cell performance when compared to diffusion losses under humid cell operation.

Impedance measurement is essential for an advanced control of fuel cells. It enables the proper operation of more sophisticated stack control and purge strategies. Furthermore, simultaneous impedance measurements enables the control of individual cells by means of micro actuators.

Acknowledgement

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