

Short communication

Effect of gas composition and gas utilisation on the dynamic response of a proton exchange membrane fuel cell

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Abstract

The transient response of a proton exchange membrane fuel cell (PEMFC) was measured for various cathode gas compositions and gas utilisations (fraction of supplied reactant gas which is consumed in the fuel cell reaction). For a PEMFC operated on pure hydrogen and oxygen, the cell voltage response to current steps was fast, with response times in the range 0.01–1 s, depending on the applied current. For a PEMFC supplied with air as cathode gas, an additional relaxation process related to oxygen transport caused a slower response (approximately 0.1–2 s depending on the applied current). Response curves up to approximately 0.01 s were apparently unaffected by gas composition and utilisation and were most likely dominated by capacitive discharge of the double layer and reaction with surplus oxygen residing in the cathode. The utilisation of hydrogen had only a minor effect on the response curves, while the utilisation of air severely influenced the PEMFC dynamics. Results suggested that air flow rates should be high to obtain rapid PEMFC response.

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1. Introduction

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy [1]. The potential of this technology lies within the transportation sector where fuel cells operated on hydrogen and air may replace the conventional internal combustion engine, thus eliminating CO₂ emissions from vehicles and increasing energy efficiency. For successful implementation in the transportation sector, the fuel cell must be able to supply a power demand that varies rapidly with time [2]. The proton exchange membrane fuel cell (PEMFC) is promising for such applications, due to its low operating temperature, high power density and system simplicity.

The power output of the fuel cell can be controlled by a well-designed power conditioning system. Instabilities in fuel cell

power due to slow processes such as cell heating and membrane humidification can be controlled by adjusting the current output of the cell. In contrast, faster processes, occurring in the sub-second time range are more difficult to compensate for. Upon rapid changes in power demand, these processes may cause power over- or undershoots which can be harmful to electronic components or cause unfavourable transient behaviour. A thorough understanding of transient processes in the sub-second time range is therefore necessary to establish design criteria for a suitable power conditioning system.

According to published literature on PEMFC dynamics, gas transport is one of the faster processes that occur in a PEMFC, beside ohmic drop and capacitive discharge. Brett et al. [3] investigated the propagation of oxygen into the gas diffusion layer (GDL) of a PEMFC and reported a response time for this process of approximately 2 s. Dong et al. [4] measured real-time gas composition in the cathode gas channel upon steps in cell voltage. The time resolution of these measurements was, however, too low to reveal the relaxation in detail, but a response time of less than 1 min was estimated. Several model studies of mass transport in the PEMFC cathode have been carried

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out [5–9], reporting response times ranging from 0.1 to a few seconds.

In a previous study from our group, we assessed the dynamic response of a PEMFC supplied with excess amounts of pure oxygen and hydrogen [10]. PEMFC response under minimal mass transport limitations was limited by a cathodic charge transfer process with a potential dependent response time. In real fuel cell applications, however, air rather than oxygen is most commonly used as cathode gas, and the utilisation of reactant gases (fraction of supplied reactant gas which is consumed in the fuel cell reaction) should be high to keep parasitic power losses low. Kim et al. [11–13] assessed the effects of fuel utilisation on transient PEMFC response with special focus on starved fuel conditions (high utilisation). At stoichiometries 1.0 and 1.2 for hydrogen and air, respectively, the increased current following from a step decrease in cell voltage could only be sustained for a certain amount of time before it decreased to a lower value due to insufficient supply of reactant gases. In real applications, a step increase in power demand must be accompanied by a corresponding step increase in fuel cell power, so gas utilisations in the range near 100% must be avoided. Kim et al. [11] also measured PEMFC response at low utilisation, showing that PEMFC response under these conditions was at least as fast as the electronic load used to control cell voltage during the step. This illustrates the importance of using a fast load and high resolution measurements when studying PEMFC response.

If reactant gases are supplied in excess (low utilisation), gas composition in the gas channels will be fairly uniform. In contrast, at high utilisation of reactant gases, most of the supplied gas is consumed in the fuel cell reaction, giving a highly non-uniform composition along the gas channel and starved conditions near the channel outlet. With this in mind, gas utilisation should be low to ensure stable fuel cell operation and optimal dynamic performance, but this entails a corresponding increase in parasitic power losses. Also, gas flow rates affect the delicate heat and water balance in the fuel cell. These considerations stress the importance of a careful selection of gas flow rates to obtain both high system efficiency and optimal dynamic performance. A detailed characterisation of PEMFC response at varying gas utilisations provides criteria for a careful selection of gas flow rates.

The purpose of this paper is to investigate how the oxygen content in the cathode gas and the utilisation of reactant gases affect the transient PEMFC response. This is done by measuring the PEMFC response to current steps at different oxygen contents in the cathode gas and varying utilisations of hydrogen and oxygen. Contrary to Kim et al. [11–13], we focus on fast transient processes, appearing in a sub-second time range. We therefore apply current steps with low switching times. We also focus on gas utilisations that give sustainable increases in power since this is essential in real applications. Three effects on the transient response are assessed: The effect of current step size at varying cathode gas compositions, the effect of cathode gas composition and the effect of oxygen and hydrogen utilisation. Such measurements provide valuable background data for an optimal selection of gas flow rates as well as design criteria for auxiliary system components and power conditioning units.

2. Experimental

2.1. Hardware and operating conditions

A membrane electrode assembly (MEA) from W. L. Gore & Associates (PRIMEA[®] MEA, Cleo Series 58, 18 μm nominal membrane thickness, 0.4 mg cm^{-2} Pt loading on both anode and cathode) was sandwiched between two GDLs from E-TEK (ELAT[®] carbon only). The geometric electrode area was 6.25 cm^2 . The MEA and GDLs were mounted in a fuel cell housing from ElectroChem (EFC05-01SP-REF) with triple serpentine flow fields. Two MEAs from the same batch were used in this study, showing only minor differences in dynamic behaviour.

The cathode was supplied with either pure oxygen (99.5% purity) or prepared mixtures of oxygen and nitrogen (99.999% purity). The oxygen content of the prepared mixtures was 60 and 21% (synthetic air). The anode was supplied with hydrogen (99.999% purity). Flow rates were set by calibrated mass flow controllers from Flow-Teknikk. Flow rates for the anode and cathode gases were chosen according to the wanted experimental conditions. Details are given in the next section.

Anode and cathode gases were humidified in separate sparge bottles. To ensure an equal and even temperature, both the PEMFC and sparge bottles were put in a heating cabinet from Termaks (TS8136). There was a substantial heat generation at high currents, so in order to keep the temperature as stable as possible, the heating cabinet was set to 40 °C unless otherwise stated. The temperature of the cathode hardware was monitored by a thermocouple from Omega[®], and the operating temperature was 41.5 ± 1.5 °C during the experiments (46 ± 1 °C for experiments in Fig. 1). We do not expect these temperature variations to affect our results significantly.

2.2. Current steps

All measurements were performed on a two-electrode setup (full cell) using an IM6e electrochemical workstation and PP200 add-on module from ZAHNER[®] elektrik. Current steps from zero to larger currents were programmed using the potentiostat software. Current step measurements on ohmic resistors showed that the potentiostat had a rise time of less than 0.1 ms. To obtain similar initial conditions before each step, the PEMFC was operated at 0.8 A cm^{-2} for at least 1 min, then the current was turned off and the step routine was started when the open circuit voltage had reached a certain value. The step routine consisted of 30 s at zero current followed by a step to a higher current which was held for another 100 s.

3. Results and discussion

3.1. Effect of current step size for different cathode gas compositions

The effect of current step size on the PEMFC response was studied with both synthetic air and pure oxygen as cathode gases. Current steps from zero to higher currents were applied, and the

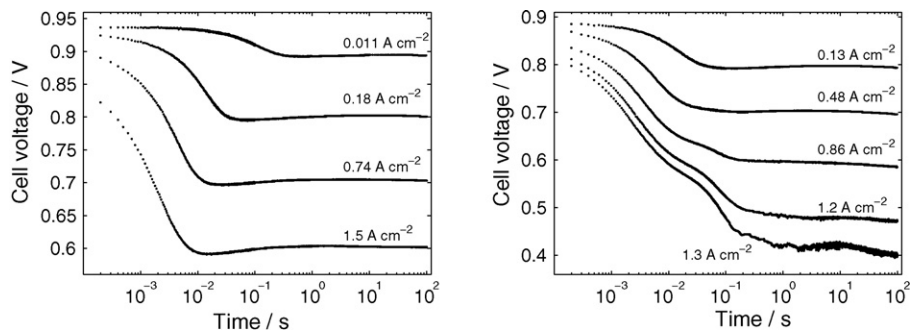


Fig. 1. Comparison of response to current steps using oxygen (left) and air (right) as cathode gas. Cathode gas flow rate was 150 (left) and 476 N ml min⁻¹ (right). Anode flow rate was 300 (left) and 200 N ml min⁻¹ (right). The corresponding utilisation of hydrogen and oxygen was thus less than 25% (left) and 32% (right).

corresponding response in cell voltage was monitored as shown in Fig. 1. The ohmic resistance estimated from the ohmic drops (not included in the figure) corresponded to the ohmic resistance of the PEMFC measured by electrochemical impedance spectroscopy. For the PEMFC supplied with oxygen (Fig. 1, left), cell voltage first decreased quickly, reached a minimum, then increased slightly for a few seconds and then decreased again, very slowly for the remaining duration of the measurement. The final slow decrease could be due to various slow responding processes, such as cathode flooding, and is not assessed further here. Two main trends for increasing final current (increasing step size) was identified for the response curves with pure oxygen: (i) The undershoot in cell voltage increased, and (ii) the response time decreased. For a step to 0.011 A cm⁻², the undershoot was 3 mV, while for a step to 1.5 A cm⁻² it was 12.5 mV. Measuring response time as the time it takes to reach the minimum cell voltage, the steps to 0.011 and 1.5 A cm⁻² had response times of 0.8 and 0.016 s, respectively. The potential dependence of the response time for a PEMFC supplied with pure oxygen was addressed previously by our group [10] and found to be related to a charge transfer process on the cathode. We do not have a satisfying explanation for the increase in cell voltage following the initial decrease at this time, but it could be related to fast improvements in local conditions, i.e. increased temperature or membrane humidity near the active sites in the cathode. Net changes in temperature and membrane water content may take several minutes, but we find it likely that local changes can appear in less than a second. Furthermore, the results of Wilson and Gottesfeld [14] suggest that the active region narrows as current density increases. Thus, for steps to higher current densities, a larger amount of heat and water is released in a smaller volume of the cathode. This may explain why the increase in cell voltage following the initial decrease becomes more pronounced with increasing step size.

When the cathode was supplied with air (Fig. 1, right), the response curves were similar in both shape and response time for the initial 0.01–0.1 s. This suggests that the initial response is related to capacitive discharge and reaction with oxygen residing near the active sites. At 0.13 A cm⁻², mass transport was not a significant limitation, and the response curves for oxygen and air were similar. For steps to 0.48 A cm⁻² and higher, mass transport limitations were seen as the onset of a second relaxation process around 0.03 s, causing a further decrease in cell voltage.

The exact time where the second relaxation appeared cannot be precisely determined from this plot, but a linear plot of cell voltage vs. time (not shown) suggested that the second relaxation appeared earlier for higher current densities. This is reasonable since surplus oxygen is consumed faster and the double layer is discharged faster at higher current densities. Between approximately 0.03 and 0.09 s the cell voltage decreased linearly with time for the three highest current densities. This can be seen as a “shoulder” in the logarithmic plot around 0.05 s (Fig. 1, right). The slope of this linear region increased linearly with current density. We are not yet aware of processes that should yield such a linear dependence and cannot give a theoretically based explanation for this behaviour at this time.

The linear voltage–time behaviour levelled out and reached a preliminary stable value after approximately 0.2 s for the step to 0.86 A cm⁻². For the steps to 1.2 and 1.3 A cm⁻² this stable value seemed to disappear in a further, more uneven decrease in cell voltage. This could be related to cathode flooding and formation/removal of water droplets from the cathode gas channel. Erratic fluctuations at 1.3 A cm⁻² indicate severely flooded cathode conditions, and a stable cell voltage at this current density could not be obtained.

In summary, increasing the current step size for a PEMFC supplied with pure oxygen gives a shorter response time due to faster charge transfer at lower cell voltages [10]. For a PEMFC supplied with air, the increased mass transport limitation imposed by nitrogen causes a further decrease in cell voltage and an increased response time.

3.2. Effect of cathode gas composition

The response curves with air and oxygen from the previous section cannot be directly compared since current values and utilisation rates were not identical for the two data sets. Therefore, another experiment was carried out to study the effect of diluting the oxygen for a chosen current step. The cathode was supplied with O₂/N₂ mixtures with 21, 60 and 100% oxygen, and a current step from 0 to 1.22 A cm⁻² was carried out for all three cathode gas compositions. To avoid oxygen starvation and large variations in cathode gas composition along the gas channel length, we chose to carry out this experiment at low gas utilisation (29%). In order to keep a constant oxygen utilisation for all compositions, the total flow rate was 476, 167

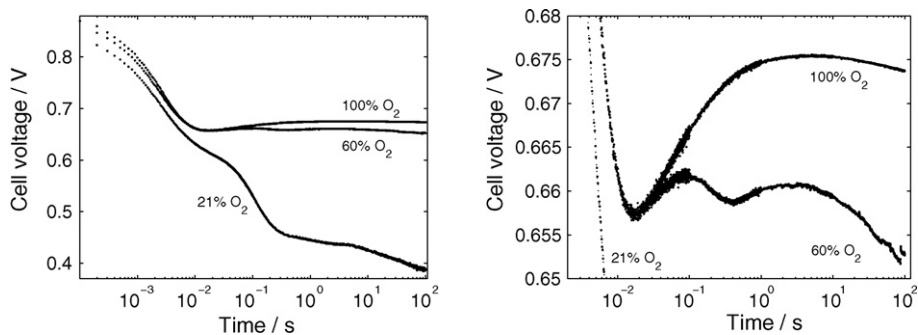


Fig. 2. Left: Response in cell voltage to a current step from 0 to 1.22 A cm⁻² for three levels of oxygen content in the cathode gas. Right: Expanded view of response curves for 60 and 100% oxygen. Gas flow rates were adjusted so that the supply rate of oxygen was 100 N ml min⁻¹ (29% utilisation) for all gas compositions. The flow rate of hydrogen was 200 N ml min⁻¹ for all compositions.

and 100 N ml min⁻¹ for 21, 60 and 100% oxygen, respectively. Higher flow rates causes a slightly higher pressure in the gas channel, and this pressure variation may affect our results. However, we expect that this effect is negligible compared to the effect of changing the gas composition.

Fig. 2 presents the cell voltage response to an identical current step at three cathode gas compositions. Reducing oxygen partial pressure had a severe impact on the PEMFC response. During the initial response (up to approximately 7 ms) a lower partial pressure of oxygen caused a lower cell voltage value, but otherwise this part of the curve was almost equally shaped for all compositions. This supports our assumption that the initial response is related to discharging of the double layer capacitance and reaction with oxygen already residing in the catalytic layer of the cathode. Effects of mass transport limitations appeared at approximately 0.04 s for the 60% curve (Fig. 2, right) and at approximately 0.01 s for the 21% curve. We assume that this time difference is a result of different amounts of oxygen residing in the catalytic layer.

After reaching a minimum at approximately 0.02 s, the response curve for 100% oxygen increased to a maximum at approximately 4 s. This effect, which could be due to local heat or water production, was commented in the previous section. The oscillations in the response curve for 60% oxygen (Fig. 2, right) are not yet interpreted nor verified from repeated measurements. The 21% curve decreased linearly with time between approximately 0.02 and 0.1 s, similar to the response curves in Fig. 1, right. A linear plot (not shown) of the response curve for 21% oxygen showed that cell voltage levelled out at a preliminary stable value at approximately 3 s.

For all compositions, a slow decrease in cell voltage was observed from approximately 10 s. This decrease was more pronounced for lower oxygen concentrations and could be related to cathode flooding. A sudden jump in cell voltage for the 60% curve (Fig. 2, right) at approximately 90 s indicates that a water plug was removed from the cathode gas channel, exposing a larger electrode area.

In summary, decreasing the amount of oxygen in the cathode gas causes an additional transient to appear at approximately 0.01 s. This transient is probably related to relaxation of oxygen partial pressure in the catalyst and GDL of the cathode and levels out in a few seconds.

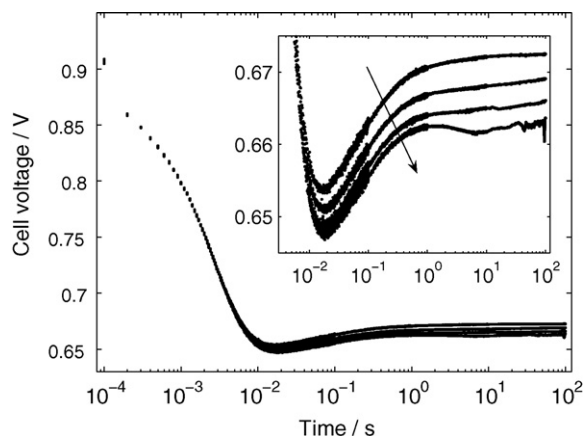


Fig. 3. Response in cell voltage to a current step from 0 to 1.22 A cm⁻² for 30, 50, 70 and 90% cathode gas utilisation for a PEMFC supplied with pure oxygen. Inset shows an expanded view of the undershoot. The arrow shows the direction of increasing oxygen utilisation. The flow rate of hydrogen was 200 N ml min⁻¹.

3.3. Effect of gas utilisation

The third variable studied in this paper is the rate of utilisation for both hydrogen and oxygen. The same current step as in the previous section (0–1.22 A cm⁻²) was applied for various flow

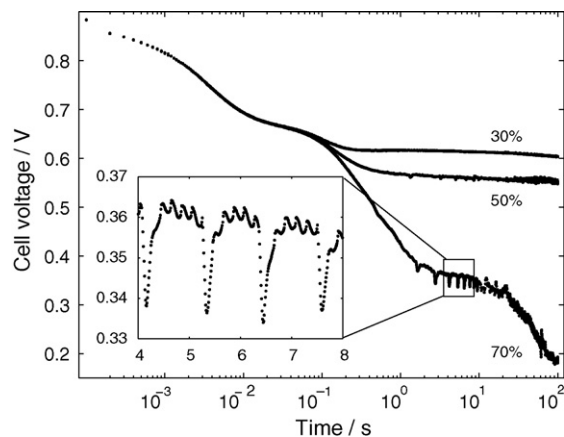


Fig. 4. Response in cell voltage to a current step from 0 to 0.80 A cm⁻² for 30, 50 and 70% oxygen utilisation for a PEMFC supplied with synthetic air. Inset shows an expanded view of the voltage dips and oscillations at 70% oxygen utilisation. The flow rate of hydrogen was 200 N ml min⁻¹.

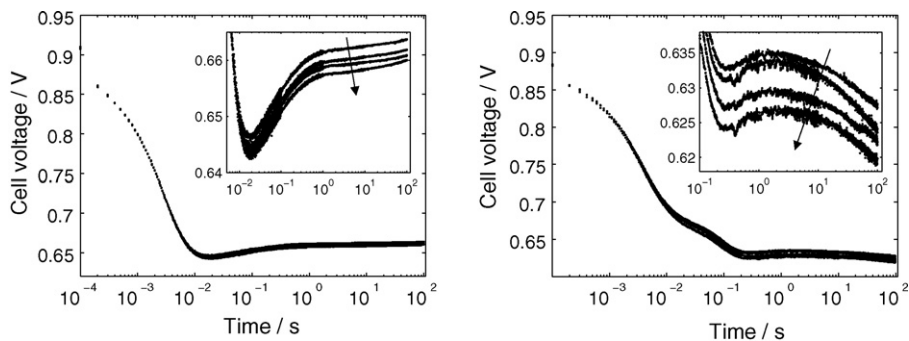


Fig. 5. Response in cell voltage to a current step for 30, 50, 70 and 90% utilisation of hydrogen. Arrows show the direction of increasing utilisation. Left: PEMFC supplied with $100 \text{ N ml min}^{-1}$ pure oxygen, current step from 0 to 1.22 A cm^{-2} . Right: PEMFC supplied with $476 \text{ N ml min}^{-1}$ air, current step from 0 to 0.80 A cm^{-2} . Insets show an expanded view of the response.

rates of oxygen or air, giving utilisation rates varying from 30 to 90%.

Fig. 3 shows the effect on cell voltage response of changing the utilisation for a fuel cell supplied with pure oxygen. The initial response (up to approximately 10 ms) was independent of utilisation rate, another indication that discharging of the double layer and reaction with surplus oxygen are dominating the PEMFC response in this time range. From approximately 0.01 s, an increased utilisation caused a shift in cell voltage towards lower values. This can be related to increasingly starved conditions along the cathode gas channel. At 90% utilisation, the voltage response started fluctuating after approximately 1 s, indicating a non-uniform distribution of oxygen along the cathode gas channel.

The effect of utilisation was also measured for a PEMFC supplied with air instead of oxygen. A smaller current step (0 to 0.80 A cm^{-2}) was imposed for these measurements since a utilisation rate of 30% at 1.22 A cm^{-2} required a higher gas flow rate than the mass flow controller could provide. Response curves for different utilisation rates are shown in Fig. 4. Increasing the utilisation had a substantial effect on the cell voltage response. Up to approximately 0.06 s the response curves were overlapping as the initial response was dominated by double layer discharge and reaction with surplus oxygen. Effects of utilisation appeared at approximately 0.06 s. A linear plot showed that cell voltage decreased linearly with time from approximately 0.03 s for all utilisations, similar to the response curves in Figs. 1 and 2. An increasing utilisation caused the linear decrease to appear in a wider time range: up to approximately 0.06 s for the 30% curve, 0.1 s for the 50% curve and 0.2 s for the 70% curve. These trends should be further assessed in future studies.

After the linear decrease, the response curves levelled out at approximately 0.3 and 1 s for the 30 and 50% curve, respectively. Thus, an increasing utilisation gave a longer response time. The 70% curve did not reach a stable cell voltage, but decreased for the remaining time of the measurement. This could be due to cathode flooding, since the flow rate and hence also the water removal rate at 70% utilisation were low. The oscillations in cell voltage (Fig. 4, inset) could be due to the dynamic behaviour of liquid water in the cathode channel. Small oscillations appear when water droplets are formed while the larger voltage dips

appear when the droplets coalesce into water plugs which are removed from the cathode gas channel.

Finally, the effect of hydrogen utilisation was investigated. Cell voltage response to identical current steps at varying hydrogen utilisation is shown in Fig. 5. Measurements were carried out with both pure oxygen and air as cathode gas. Increasing the hydrogen utilisation mainly decreased the cell voltage by a few millivolts, similarly to the effect of an increasing utilisation of pure oxygen (ref. Fig. 3). The shape of the response curves was otherwise not significantly affected. Compared to the effect of increasing the oxygen utilisation in a PEMFC supplied with air, the effect of hydrogen utilisation was minor. This is an encouraging result, since hydrogen utilisation should be high to obtain high fuel efficiency and low parasitic power losses.

In summary, for a PEMFC supplied with pure gases, an increasing gas utilisation shifts the dynamic cell voltage response to lower values after approximately 0.01 s. For a PEMFC supplied with air, the same effect is seen for an increasing hydrogen utilisation, while an increasing oxygen utilisation causes a further decrease in cell voltage and a longer response time.

4. Conclusion

Results suggested that the initial PEMFC response up to approximately 0.01 s is determined by capacitive discharge of the charge double layer and reaction with surplus oxygen residing in the cathode. Increasing the current step size for a PEMFC supplied with pure oxygen gives a shorter response time due to faster charge transfer at lower cell voltages. Decreasing the amount of oxygen in the cathode gas causes an additional transient to appear at approximately 0.01 s. For a PEMFC supplied with air, this additional transient levels out in a few seconds.

Increasing the oxygen utilisation for the PEMFC supplied with air has a major impact on the transient PEMFC response. Thus, to obtain a fast response to current steps, oxygen utilisation should be kept low, but this consideration must be balanced against the increased parasitic power loss at high flow rates. For a PEMFC supplied with pure hydrogen and oxygen, an increasing gas utilisation shifts the dynamic cell voltage response to lower values after approximately 0.01 s, but does not affect the shape of the response curves.

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