Oscillation of Polymer Electrolyte Membrane Fuel Cells at Low Cathode Humidification

Daniel G. Sanchez[1], K. Andreas Friedrich[1]

[1] Deutsches Zentrum für Luft und Raumfahrt (DLR), Institut für Technische Thermodynamik, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany.

ABSTRACT

Oscillatory fluctuations of a single proton exchange membrane fuel cell appear upon operation with a dry cathode air supply and a fully humidified anode stream. Periodic transitions between a low and a high current operation point of the oscillating state were observed. The transition time for the change from the low to the high operation is fast and does not depend on the operating parameters, while the downward transition depends strongly on the operating conditions. An insight into the transitions is obtained by current density distributions at distinct times indicating a propagating active area with defined boundaries. The high current operation possesses a high electro-osmotic drag and a high permeation rate (corresponding to liquid-vapor permeation) leading to a large water flux to the cathode. Subsequently, the liquid reservoir at the anode is consumed leading to an anode drying. The system establishes a new quasi-stable operation point associated with a low current, low electro-osmotic drag coefficient, and a low water permeation (corresponding to vapor-vapor permeation). When liquid water is formed at the anode interface after some time the fast transition to the high current operation occurs due also to a flooding effect leading to blockage of channels.

Palabras clave: Polymer electrolyte, Fuel cell, Water management, Oscillations.
Keywords: Polymer electrolyte, Fuel cell, Water management, Oscillations.

1. INTRODUCCIÓN

Proper water management is of paramount importance for proton Exchange membrane fuel cell (PEMFC) since performance losses are known to result cathode flooding, gas dilution or membrane dehydration. As a consequence, water management is one of the most important issues for successful operation, high performance and durability of PEMFC. An insufficient level of humidification lowers the ionic conductivity in the membrane and results also in a performance reduction. From the system point of view the necessity to ascertain a well-humidified membrane and concurrently to avoid condensation of liquid water adds to significant complexity. Numerous studies have investigated the operation of PEMFC under dry conditions to simplify operation. This contribution investigates the oscillatory fluctuations observed when operating a single polymer electrolyte fuel cell with dry air. This oscillation state consists of two distinct operation performances of the cell which are investigated as a function of operation conditions recording the local current density distributions. The transition time from low to high performance is mostly operation independent; in contrast to the transition from high to low current which depends strongly on the experimental conditions. We discuss the possible sequence of the processes leading to the oscillatory fluctuation.

2. PARTE EXPERIMENTAL

The investigation of the dynamic response of polymer electrolyte fuel cells at reduced temperatures was performed on single cells with an electrode area of 25 cm^2 at the testing stands of the German Aerospace Center (DLR). The test bench is home-made and is controlled by programable logic controllers (PLC), which allow an automatic control of the input and output conditions, such as pressure, temperature, flow rate of gases, humidity of reactants. The relative humidity of the inlet gases was controlled through water-filled heated sparger bottles. Lines between humidifiers and the fuel cell were heated in order to avoid water condensation. The gas mass flow rates were regulated at the fuel cell inlets whereas the pressure was controlled at the outlets. The pressure was fixed for the experiment at constant value of 1500 mbar. The flow of gases (air and H_2) is controlled through the test station and can be varied between 0 to 500 ml min^{-1} on the anode side and between 0 to 2000 ml min^{-1} on the cathode side. The reference operating conditions are summarized in Table 1.

These testing stations have the possibility to by-pass the bubblers and introduce dry gasses into the cell. We use the normal way of defining the relative humidity (RH).

Table I: Reference operating conditions in this study

Cell temperature	T = 70 °C
Temperature of anode bubbler	80ºC, nominally RH=152
Pressure	P = 1.5 bar
Hydrogen stoichiometric ratio,	$\lambda_{H2} = 1.4$
Air stoichiometric ratio	$\lambda_{Air} = 2$
Humidification	Dry Air Hydrogen humidified at 100 % RH or under condensing conditions
Flow rates	Varying

A relative humidity of 0 % was applied to the cathode side which is accomplished by introducing ambient gas using the bubbler bypass. A commercial MEA was used produced by Ion Power Inc. Company.
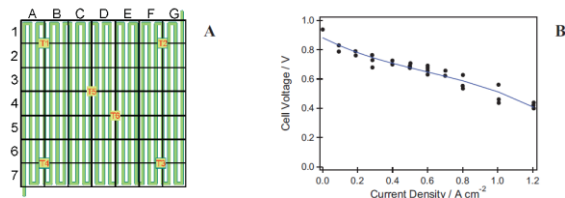

Figure 1. (A) Segment distribution of a flow field arrangement with temperature sensors and single serpentine channel flow field. (B) Initial U(i) curve of Nafion®111-IP at reference conditions with full humidification.

Current density measurements in single cells have been developed at DLR. A segmented bipolar plate based on printed circuit board (PCB) technology with integrated temperature sensors was used in the single cell to analyze the locally resolved current density distributions (2, 3), has been introduced at the anode side. A single serpentine channel for the humidified anode and for the non humidified cathode was used to ensure that no partial blocking of the flow field by liquid water is possible. The current density distributions were classified as depicted in figure 1 (A).

Flow configurations are presented which provide different results:

- Configuration A (co-flow): Anode: input G1 output A7 / Cathode: input G1 output A7
- Configuration B (counter flow): Anode: input A1 output G7 / Cathode: input G1 output A7

3. RESULTADOS Y DISCUSIÓN

Oscillating fluctuations of PEMFC single cells were observed under dry operation at the cathode and high humidification at the anode and were further investigated to understand this phenomenon. The cell was first operated in the flow configuration A (co-flow) under condensing conditions at anode and full humidification at cathode giving an adequate power density, see figure 1 (B). Then the humidifier

was by-passed at the cathode reducing instantaneously the cathode humidity to dry conditions in the cell compartment. The current is recorded versus time (ca. 2.7 h) in figure 2 at a constant cell voltage of 500 mV under dry cathode operation and a nominal humidity of 152 % at the anode. This relative humidity > 100% indicates condensing conditions with liquid wáter present at the anode. At first the current density decreases somewhat from 650 mA cm^{-2} to about 610 mA cm^{-2} within 1000 s, then a fluctuation with increasing amplitude is observed which is followed by a continuous oscillating fluctuation between ca. 610 mA cm^{-2} and ca. 60 mA cm^{-2} with a gradual decrease of current due to degradation of cell performance. A periodicity of the fluctuation is evident although some irregularities in the oscillation are present.
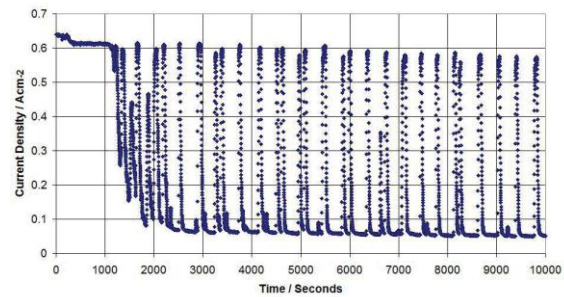

Figure 2. Instabilities of a single cell operated with a dry cathode feed (RH=0%) and a wet anode at nominal RH = 152%, cell voltage 500 mV; FH2 = 180 ml min^{-1}, Fair = 560 ml min^{-1}, co-flow configuration.

What is apparent from this measurement is that the fluctuation consists of two operation performance points that are stable for some time. The system is oscillating between them. For these operating conditions the low current regime has a longer residence time of 300 s than the high current state which is constant for about 50 s. The amplitude and also the frequency of the oscillations depend on the operating conditions and the RH value at the anode. It is important to emphasize that no oscillating fluctuations are observed when both gas feeds at anode and cathode are dry. This observation already points toward the importance of the cell wáter balance for the oscillatory response of the cell. The transition between the low current operation point and the high currents takes about 20 s. The high current point of the oscillation is stable for ca. 50 s with a small change of current and then a transition to the lower performance operation is observed.

It is normally assumed that the slowest process at the cell level is membrane hydration with time constants in the range of at least 20 – 25 s.

The observed transition times here are in the lower range associated with hydration effects and it is

interesting to understand how a macroscopic area of 25 cm^2 is affected.

From here we define (L) for low current state, and (H) for hight current state.
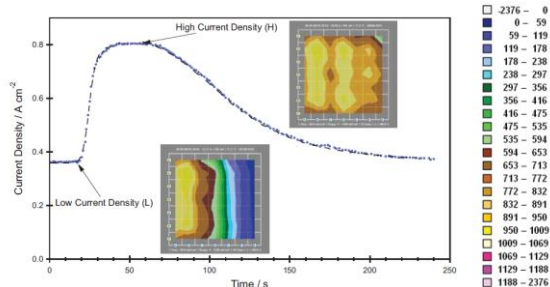

Figure 3. Transition from low to high current state and consecutive decay for counterflow configuration B at cell voltage of 500 mV, Fair = 660 ml min^{-1}, FH2 = 200 ml min^{-1}, cell temperature Tcell = 70 ºC. Right hand side: Color representation of current densities.

Therefore, the current density distribution with 49 segments for the transition at co-flow and counterflow are investigated. The associated measurements are displayed in the figures 4 and 5. Figure 3 shows a fluctuation in a counter-flow configuration. With this configuration the stability of H is favored. The higher stability is evident from a much slower decay of H to L in the order of hundreds of seconds. This compares to about 20 s rise at the upward transition. In addition the amplitude change between L and H is significantly less than in the co-flow case.
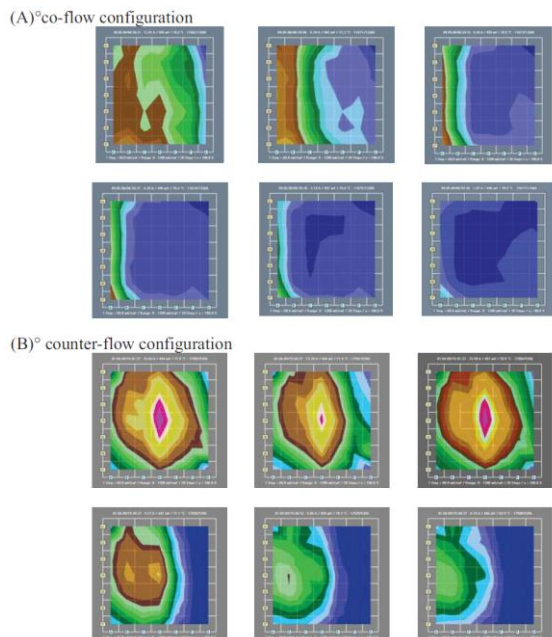

Figure 4. Current density during the downward transition from the high current to the low current state. cell voltage Ucell = 500 m V, (A) co-flow configuration with total time of 30 s from first to last image, (B) counter-flow configuration with total time of 150 s from first to last image.

Interestingly, the upward transition shows the same characteristic time as in the co-flow configuration. The associated current density color plots are provided in the insets of the image showing a homogeneous current density distribution at H associated with a low ionic resistance, high humidification and presence of liquid water at the anode. For L the current density distribution is inhomogeneous with some high current densities remaining at the anode inlet (corresponding to cathode outlet location) and low current densities at the cathode inlet.
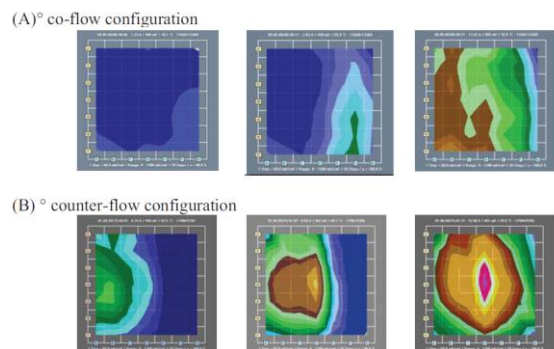

Figure 5. Current density distribution during the upward transition from the low current to the high current state. Cell voltage Ucell = 500 mV, (A) co-flow configuration, (B) counter-flow configuration, the total transition is around 20s.

From these observations it is clear that the area with high current density changes during the transitions and the current density distribution depends on the flow configuration which are shown in figures 4 and 5. The counter-flow configuration is of advantage regarding performance (high current operation stability) and exhibits a propagating active area with a boundary during the transitions. The downward transition starts at dry side of the cell area (cathode inlet) and the upward transition starts at the wet cell area (cathode inlet) and the upward transition starts at the wet side (anode inlet).
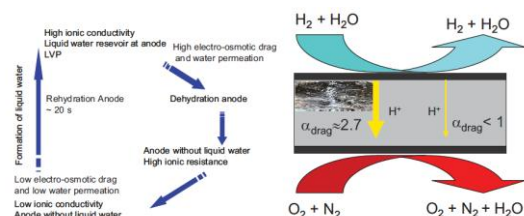

Figure 6. Left: scheme for the explanation of the transition between high current and low current states; right: Schematic for depicting the membrane processes in the two cell states.

Summarizing the observed effects it is evident that the observed operation points and the transitions between them are a consequence of the wáter balance of the membrane or the interface area. This transition is strongly affected by the flow

configuration (counter-flow versus co-flow) and by the flow rates at anode and cathode.

Based on the operating conditions it can be assumed that during most of the time no liquid water is present at the cathode for all conditions even if reaction water and electro-osmotic drag are added.
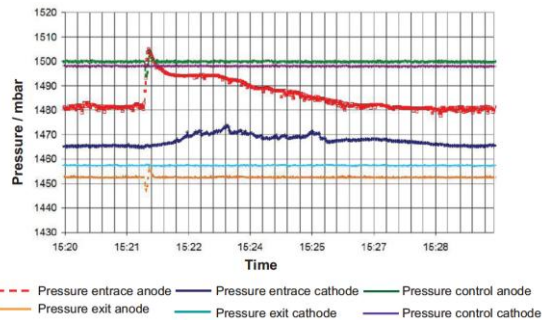

Figure 7. Pressures in the cell during the ignition event, namely the L to H transition.

This was not the case for the anode side which was exposed to high humidity. The observed transitions in the fluctuating state were induced by a changing humidity at the anode associated with varying water transport properties (mainly the electro-osmotic drag coefficient and water permeation rate). The changes of water transport rates resulted in a strong positive feedback mechanism represented in figure 6. In the H operation liquid water is present at the anode, resulting in a well-humidified membrane interface which possesses a high electro-osmotic drag coefficient and high water permeability. The high drag of water from anode to cathode and the effective removal of water at the dry cathode feed reduce the liquid water present at the anode until a drying of the membrane from the anode side starts. This is expected when the anode water reservoir at the interface is totally consumed starting from the dry anode outlet region. This leads to an increase of the low current area from the anode outlet until the whole area is in the low current point with dry anode and cathode conditions. With the low current and low water content in the membrane the electro-osmotic drag coefficient drops below 1 and the interface are dry. electro-osmotic drag and low permeation decreases the water transport from anode to cathode dramatically. Under these conditions the current density is just 50 mA cm^{-2} corresponding to L operation. The electro-osmotic drag coefficient is in the order of 0.5- 0.6 leading to a value of ca. $r_{H2O, EOD} = 4*10^{-7}$ mol cm^{-2} s^{-1} transported to the cathode and the vapor-interface rate ($r_{H2O} \approx 1*10^{-6}$ mol cm^{-2} s^{-1}) is an order of magnitude lower compared to liquid-interface permeation. Under these conditions the water influx at the anode is not removed by current flow and liquid water can start to accumulate. The liquid water first forms at the anode inlet because the humidity is expected to

diminish along the anode channel due to the water uptake of the membrane. Therefore the first highly conductive area forms at the anode inlet for all flow configurations. As soon as liquid water forms liquid-interface conditions lead to high water transport properties at the anode interface and concurrently the transition from low current to high current is induced. The "ignition" event, namely the transition from L to H is determined by the presence of liquid water a blocking phenomenon plays an important role as seen from the time dependent pressures shown in figure 7. Just before the transition pressure at the anode inlet rise by about 25 mbar and with a delay also a pressure increase is observed at the cathode inlet. Small changes at the outlet pressures are neglected here. A transient increase in pressures is consistent with liquid water formation and a blocking of the channel. This blocking effect of liquid water is speculated to increase water transport to the cathode so that part of the cathode is also exposed to liquid water thus triggering the fast increase in conductivity leading to the H level.

4. CONCLUSIONES

This work shows results concerning the appearances of oscillatory fluctuation when the cathode is dry and the humidity level at the anode high. It is observed that for specific operating conditions a fluctuating state exists with two operation points with characteristic high and low currents. Periodic transitions between these states are observed. The upward transition between the low to the high current operation is faster compared to the downward transition with a characteristic time of 20–25 s. The downward transition depends strongly on the operation parameters and the following trends are observed which favor the high current operation:

- Higher humidity at anode (especially water condensingconditions).
- Lower cathode flow.
- Counter flow configuration.

Bibliografía

1. F. N. Buchi et al, J. Electrochem. Soc. 144, 2767 (1997).
2. E. Gülzow, et al, J. Power Sources 86, 352 (2000).
3. M. Schulze et al, J. Power Sources 173, 19 (2007).