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Long term testing of start-stop cycles on High Temperature PEM Fuel cell stack

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Abstract

A PEM fuel cell with an operating temperature above 100 °C is desired for increasing the kinetics of reactions, reduced sensitivity to impurities of the fuel, as well as for the reduction of the requirements on thermal and water management systems. High Temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFC) can effectively be combined with CHP systems to offer a simple system design and higher overall system efficiencies. For HT-PEMFC systems, the development of elaborated start/stop strategies is essential in mitigation of fuel cell degradation during these events. A 5 cell co-flow stack is assembled with BASF P1100W membrane electrode assembly (MEA) with an active area of 163.5 cm². Continuous operation and more than 1,500 start stop cycles have been performed in order to study the degradation effects of both continuous operation and of repeated start stops using a protective start-stop algorithm, which is designed to avoid the formation of aggressive cell potentials. The repeated use of this procedure led to a degradation of 26 µV/cycle at a current density of 0.25 Acm⁻² and 11 µV/cycle at a current density of 0.03 Acm⁻². At open circuit voltage (OCV), a higher degradation rate of 133 µV/cycle was observed.

Keywords: High temperature PEM fuel cell, PBI/H₃PO₄, Performance degradation, Start-stop, Long Term Testing
1. Introduction

In consideration to ecological and energy issues, there is a tendency for transition towards hydrogen energy which assumes wide use of fuel cells for both transport and stationary applications. For allowing a commercial use of these technologies, certain lifetime requirements have to be fulfilled, which is still a developmental issue for some of the possible HT-PEMFC applications. The US Department of Energy (DOE) provided recommendations of about 40,000 hours of operation for stationary applications and 5,000 hours of operation for mobile applications, which leads to a request of a very limited performance decay. Thus, the degradation of fuel cell components plays a vital role in the performance and lifetime of the fuel cell. Optimal parameters need to be found out in order to operate the fuel cell at its full potential and there involves a significant challenge in improving the lifetime of the HT-PEM fuel cells. Optimization of operation strategies is quite essential in mitigation of fuel cell degradation during start-stop events. Therefore, a profound knowledge both about the influence of decisive operating parameters and the involved degradation mechanisms is required.

For the development of high temperature PEM Fuel cells, significant attention has been focused upon fundamentally understanding degradation and in development of strategies to improve fuel cell durability. The start-up strategy developed by Shen et al. [1] includes a nitrogen purge of the anode prior to the introduction of the hydrogen fuel. This strategy resulted in low potential difference between the cathode and the anode, which implies lower carbon corrosion by localized corrosive potentials. Shen et al. [1] further found that if a fuel/air boundary cannot be avoided, an introduction of fuel at a higher flow rate was preferable. The higher flow rate still results in a high potential difference, but during a shorter time, which reduces the carbon corrosion.
Another start-up strategy was developed by applying a dummy load as the fuel fills the anode compartment [1-3], where the dummy load lowers the potential difference and thus carbon corrosion is avoided. This type of voltage control reduced the degradation from ~100 μV/cycle to ~4 μV/cycle in a test conducted by Perry et al. [3]. A third strategy has been tested by Jo et al. [4], where the hydrogen is supplied to the anode prior to the introduction of oxygen on the cathode side. This strategy resulted in decreased power loss and a reduced electrochemically active catalyst surface area loss.

Shutdown strategies have also been developed to improve the durability of fuel cells. Kim et al. [2] tested a nitrogen purge strategy on the anode that lowered the potential difference at shutdown and reduced degradation of the MEA. Dummy load strategies where the remaining hydrogen is consumed before shutdown have been developed [1, 3]. The dummy load reduces the cell potential which limits the carbon corrosion.

After 244.5 hours of OCV tests carried out by Qi and Buelte [5], the crystallite size of cathode Pt increased to as much as 5.3 times of its original value and observed a decline with most of the loss occurred in the first 50 hours of exposure to OCV due to the significant increase in cathode activation resistance and the mass transport resistance.

Mocotéguy et al. [6] tested a single cell and 24 cells stack 500 W_el. with constant current density of 0.2 Acm⁻² and 0.4 Acm⁻² and 160 °C over a total of 500 h, including additional sections with dynamic operation under simulated reformate and air with respective hydrogen and oxygen over-stoichiometric ratios of 1.4 and 2. After 500 hours of operation, the degradation rate of the single cell ranged from 41 to 149 μVh⁻¹, whereas the 24 cell stack after 658 hours of operation was stopped due to worst cell performances. The ageing effect also strongly varied with dependence on cell position with some cells exhibiting an average degradation ranging around 20 μVh⁻¹, while some others exhibited degradation rates above 100 μVh⁻¹.
Long term stability of PBI-based HTPEMFC has been demonstrated for more than 17,000 h under steady state condition \((T = 150 \, ^\circ \text{C}, \lambda_{\text{H}_2} = 1.2, \lambda_{\text{air}} = 2, \, i = 0.2 \, \text{Acm}^{-2}\), with pure hydrogen and air) with a voltage decay rate of around 10% during a single cell test. Oono et al. [7] discovered that the degradation is due to aggregation of the electrode catalyst particles in the early stages, and due to the depletion of phosphoric acid in the latter stages.

Based on the commercial Celtec-P1000 MEA, Schmidt and Baurmeister [8] reported 11 μVh^{-1} degradation rate after a period of 6,300 hours with 260 cycles (a 12 h operation at 160 °C followed by 12 h shutdown period) under mild conditions operation at 160 °C on hydrogen and air with respective stoichiometric ratios of 1.2 and 2. Start/stop cycles did not impact significantly the cell ohmic resistance or the oxygen reduction kinetics but ohmic resistance slightly increased beyond 2,500 hours of ageing. Mass transfer limitations at the cathode increased with ageing and were magnified by the start/stop cycling.

During dynamic tests with thermal, load and shutdown-startup cycling, the amount and the vapor pressure of the water product varies and thinning of phosphoric acid might be involved. In addition, the shutdown-startup or/and temperature cycling cause thermal and mechanical stresses to the membranes and cell components as well as the volume expansion and contractions of the acid in MEAs. Another important mechanism of the cell degradation involved in these dynamic tests is the corrosion of carbon support and sintering of noble metal catalysts [9].

In this paper, we have studied the impact of start/stop cycling induced performance degradation of a 5 cell Celtec-P 1100 W stack under the conditions of CHP applications for 1,562 cycles. A protective start-up and shutdown strategy has been chosen in order to increase the lifetime of the fuel cell. After activation, the stack is progressively operated according to the protective start-stop algorithms shown in section 3.1. The algorithms for analyzing the fuel cell degradation are also presented in the following section.
2. Experimental procedure

This section explains the experimental setup and equipment used for testing the aging of fuel cells. A 5 cell co-flow stack with an active area of 163.5 cm² is assembled using BASF P1100W MEAs. A leakage test using forming gas (95% Nitrogen, 5% Hydrogen) showed overall leakage rates of less than 7 Nml min⁻¹.

2.1 Fuel cell test bench

For the characterization of both performance and degradation of the fuel cell stack, a test bench with additional capabilities for gas analysis has been used. The test bench is equipped with:

- Flow controllers for hydrogen (5 Nl min⁻¹), nitrogen, carbon dioxide (anode side) and air (20 Nl min⁻¹), oxygen and nitrogen (cathode side).
- Mass spectrometer (Pfeiffer GSS 300) for measurement of inlet and outlet gas concentrations for both anode and cathode side.
- Thermo oil based heating and cooling system (Julabo HC) for active cooling and stack heating up to a temperature of 200 °C.
- Electronic load (Höcherl & Hackl DS 1006) for adjustment and measurement of both cell voltage and current.
- Yokogawa data acquisition system with 30 individual channels and 8 Hz maximal acquisition frequency for single cell voltages.
- SIEMENS PLC 200 unit for test bench control and measurement of flow rates and temperatures, including proprietary data acquisition and control software (start/stop, characteristic curve recording under galvanostatic or potentiostatic control, constant power operation, gas flow control for constant media utilization, minimum gas flow rates, temperature control, data storage).
2.2 Fuel cell test and operation procedures

Heat up of the stack is performed with a rate of 2.5 K min\(^{-1}\) under nitrogen (N\(_2\)) purge to avoid start-stop induced carbon corrosion. During operation, simulated reformate (H\(_2\)/CO\(_2\)/CO 74.8/25/0.2 Volume % or H\(_2\)/N\(_2\) 80/20 Volume % mixture) was used as anodic fuel at a minimum gas flow rate equivalent to a stoichiometric ratio of 1.25 (anode) and 2.5 (cathode) at a current density of 0.25 Acm\(^{-2}\) throughout the experiment to improve the repeatability and to ensure the reliability of the results. Reactant gases were kept dry throughout the experiment.

The voltage at the given current density was recorded for 3 minutes and determined by the average value excluding transient periods. However, the stay duration at lowest current densities and at OCV was limited to 1 minute to avoid cell degradation caused by high cathodic potentials.

3. Results and Discussion

Before starting with degradation tests, the stack had been activated and operated for 120 h. Polarization curves were recorded under H\(_2\)/N\(_2\) and H\(_2\)/CO\(_2\)/CO mixture, which are shown in figure 1. The stack had an initial output power at 0.4 Acm\(^{-2}\) of 188 W (H\(_2\)/N\(_2\)) and 185 W (H\(_2\)/CO\(_2\)/CO). The decrease in performance associated with a fuel switch from H\(_2\)/N\(_2\) to reformate remains below 2 % irrespective of the applied current density.
**3.1 Start-stop cycling**

The stack is heated at a rate of 2.5 K min\(^{-1}\) under nitrogen flow on anode side and “no flow” condition at cathode side. As the stack reaches 115 °C, fuel flow is started on the anode side followed by cathode air flow after 30 seconds. The stack is operated at open circuit voltage (OCV – Point “a” in figure 2) for 30 sec, and then current is ramped up to 0.25 Acm\(^{-2}\) in 90 seconds. This current is kept until 900 sec (point “b” in figure 3) after a stack of 165 °C is reached. Then the current is stepped down to 0.03 Acm\(^{-2}\) for 600 seconds (point “c” in figure 3) which allows the stack to cool down. The stop procedure is initiated by the shut off of the air flow at the cathode which reduces the voltage close to zero. After 60 seconds the anode flow is switched to nitrogen and then, the stack is cooled down back to 80 °C by turning off the oil pump. The three data points from start stop algorithm shown in Figure 2 and 3 are analyzed for cell voltage degradation. The stack is operated for 4,160 hours, including 4,042 hours (1,562 cycles) of start/stop cycling with 430.6 hours (170 cycles) under hydrogen nitrogen mixture and 3,612 hours (1,392 cycles) under reformate. Of these 1,562 cycles 24 cycles weren’t recorded with data acquisition system, and are thereby not included in Figures 4, 5 and 6. Emergency shut-downs were performed due test bench reasons after 1,264 h and 4,110 h of operation.
Figure 2: Startup cycle with applied current density, as function of fuel composition and temperature

Figure 3: Shutdown cycle with applied current density, as function of fuel composition and temperature
(a) OCV Degradation

During initial cycles, a stable voltage of 0.93 V was observed for the initial 62 cycles, followed by slow decline. For the next 100 cycles, the worst performing cell showed a slightly fluctuating performance. During this phase, data logging was inactive over 24 cycles (not shown in the diagram). After the first 186 cycles, the results showed more or less a steady decline of appr. 133 μV per cycle which is shown in figure 4. In this period of 1,376 cycles the OCV loss is significant compared with that of performance under load state. Figure 4 indicates a small crest in performance at cycles 10, 440, 1,266 and 1,522 respectively due to operation at high current density of 0.45 Acm\(^{-2}\) during the polarisation curve operation. The experiment is stopped shortly after that time because open circuit voltage fell below 0.7 V for the worst cell. It is assumed that most of the OCV degradation is due to reduced gas tightness over time, since other effects like reduction of electrochemical surface area and carbon corrosion not mainly affect the OCV.

![Figure 4: OCV degradation during start-stop cycling (120 °C stack temperature)](image-url)
(b) Degradation at 0.25 A cm\(^2\)

The first 9 cycles were performed under hydrogen-nitrogen mixture and then fuel is switched to reformate flow. The averaged cell voltage during the initial 54 reformate cycles performed stable or slightly increasing around 0.63 V at a current density of 0.25 A cm\(^2\). Specially, the worst cell showed some increase in performance during these cycles. Then the voltage started to decline in a semi logarithmic behaviour till cycle 964 as shown in Figure 5 where the anodic fuel flow is switched to hydrogen-nitrogen mixture. The voltage decay followed the same semi logarithmic behaviour irrespective of fuel until cycle 1,125. After that time, reformate was re-applied leading to a small voltage drop then recovered followed again by slightly increased voltage decay until end of test (1,562 cycles). In general, cell operation under hydrogen-nitrogen mixture showed a slightly higher cell voltage (< 10 mV) than under reformate. The voltage peak at cycle 371 is due absence of carbon dioxide during that cycle due to a test bench reason. The overall voltage degradation (measured between cycles 1 to 1,562) accounts to 26 µV per cycle.

![Figure 5: Voltage degradation during start-stop sequences at a current density of 0.25 A cm\(^2\)](image-url)
(c) Voltage Degradation at 0.03 A cm$^{-2}$

The average single cell voltage remained steady for initial 60 cycles, and then it started to decline gradually till the cycle 964. The anodic flow change to hydrogen nitrogen mixture showed a slight hike in voltage, which stayed almost constant from cycle 965 to 1,124. The fuel is reverted back again to reformate at cycle 1,125, which also showed small boost in voltage and stayed constant for the next 60 cycles followed by slow exponential decline till the end of the experiment. Figure 6 elucidates the overall decay in performance accounts to 11.2 µV per cycle (measured between cycle 1 and 1,562). Tables 1a and 1b present the overview of voltage during initial cycles and voltage degradation after cycling.

![Figure 6: Voltage degradation during start-stop sequences at a current density of 0.03 A cm$^{-2}$](image_url)

Measured cell voltages and degradation rates for all single cells are summarized in Table 1.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Initial Voltage [V]</th>
<th>Degradation [µV/Cycle]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OCV</td>
<td>0.25 Acm$^{-2}$</td>
</tr>
<tr>
<td>Cell 1</td>
<td>0.936</td>
<td>0.598</td>
</tr>
<tr>
<td>Cell 2</td>
<td>0.921</td>
<td>0.609</td>
</tr>
<tr>
<td>Cell 3</td>
<td>0.942</td>
<td>0.615</td>
</tr>
<tr>
<td>Cell 4</td>
<td>0.929</td>
<td>0.607</td>
</tr>
<tr>
<td>Cell 5</td>
<td>0.943</td>
<td>0.608</td>
</tr>
<tr>
<td>Ave</td>
<td>0.934</td>
<td>0.607</td>
</tr>
<tr>
<td>Min</td>
<td>0.921</td>
<td>0.598</td>
</tr>
<tr>
<td>Max</td>
<td>0.943</td>
<td>0.615</td>
</tr>
</tbody>
</table>

Table 1: Single cell voltage of the stack (a) voltage before stack ageing (b) voltage degradation
3.2 Continuous operation

For comparison, we operated a 12 cell HT-PEMFC stack with same MEA selection for more than 1,600 h. The operation conditions were same as described in chapter 2.2. The resulting performance over time is shown in figure 7. The overall degradation rate turned out to be 13.25 µV/h. The start stop degradation data at 0.25 Acm\(^{-2}\) provided in Table 1 lead to a degradation rate of 10.2 µV/h, which is even lower than the degradation rate obtained during continuous operation. On the other hand, cooling down and heat up times under nitrogen are included there, such that this number should not be over interpreted. Nonetheless, this comparison shows that the developed start stop procedure applied leads to very small additional degradation effects.

![Figure 7: Voltage degradation during continuous operation of a 12 cell stack at a current density of 0.25 Acm\(^{-2}\)](image-url)
3.3 Polarization Curves

Figure 8 presents the evolution of stack current voltage curves after 9, 463, 1,289 and 1,562 cycles of start-stop, corresponding to the operating times of 120 h, 1,290 h, 3,402 h, and 4,042 h respectively. The first characteristic curve is performed after 9 cycles of hydrogen-nitrogen mixture and therefore showing highest performance. In general, a downward shift of the complete curve from the beginning of cycling to the end of cycles has been observed. The second curve however, is inhomogeneous due to the case that it is performed after a stack shutdown and had not fully recovered temperature wise in the low current density region. In the last two curves (at 3,402 h and 4,042 h) there is a significant voltage decay at OCV condition which is presumably due to an increased gas crossover from anode to cathode.

![Figure 8: Characteristic current voltage curves after corresponding operating hours](image)
3.4 Analysis of degradation effects

The interpretation of polarization curves shown in figure 8 let us conclude that two main effects contribute to the observed degradation. First, the OCV degradation seems to be more prominent than the degradation under current flow. This effect is presumably due to a certain loss of gas tightness of the MEA during the last phase of test (3,402 to 4,042 h). The current density reduction over the entire operation time e.g. at 0.65 V from 0.18 Acm² to 0.07 Acm² corresponds to a factor of appr. 2.6. An estimation based on IR-corrected values (not shown) leads to a corresponding factor of 3.75. CV experiments showed a factor of Pt surface area change between 120h and 4042 h of 4.25. These results provide an indication that the major part of degradation may be attributed to both Pt surface area loss and loss of gas tightness. A post situ analysis of the membrane thickness of both new reference samples (av. thickness 120 µm) and used membranes showed only small thinning effects of appr. 10 µm.

4. Conclusions

In this work, a high temperature fuel cell stack with 5 cells based on PBI/H₃PO₄ has been tested for 1,392 cycles of start-stop operation under reformate and 170 cycles under hydrogen, corresponding to a total of 4,160 operating hours. The longest uninterrupted test run is done for 524 cycles which is around 1,342 hours. The accumulated hours at OCV (appr. 13 h in total) is expected to have a significant negative impact on cell degradation, resulting in a higher voltage decay rate, presumably caused by carbon corrosion and electrochemical surface area loss. Therefore OCV operation should be avoided to extend the life of high temperature PEM fuel cells. In spite of these OCV times leading to an additional degradation, quite attractive values for the degradation per cycle could be achieved by the use of an appropriate start stop procedure as described above. The degradation rates per cycle are ranging between 11 µV/cycle at a current density of 0.03 Acm² and 26 µV/cycle at 0.25 Acm². At OCV, degradation rates observed are about 5 times higher than that of
operating with a load of 0.25 A cm$^2$. It should be emphasized, that the provided data results on a repeated start/stop and current density cycling, and provided thereby the effect of the procedures applied to an operation of the stack at the current densities investigated and discussed. Moreover, it should be stressed that the provided operating time data may mislead to shorter lifetime expectations. For continuous operation, a degradation rate of 13.25 µV/h has been determined. On the other hand, if e.g. one daily start stop is performed by the system, a life time of appr. 4 years (due to start stop degradation effects) could be expected. So, the contribution of continuous operation to degradation is expected to be even higher than the contribution of one daily start stop. Taking the high number of cycles performed into account, the start stop cycle performed can be considered as a low degradation cycle concerning carbon corrosion and catalyst surface area loss. On the other hand, a strong “wet/dry” cycling has been performed by the repetition of normal operation (“wet” condition) followed by a longer period of nitrogen purge (“dry” condition). This kind of cycling is stressful to the membrane as well as to the membrane subgasket interface due to mechanical stress/strain effects and may explain the high degradation under OCV. Future work will be to implement this start-stop strategy in a combined heat and power units and validate it for the durability of the system.

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