Think Different! Carbon Corrosion Mitigation Strategy in High Temperature PEFC: A Rapid Aging Study

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In a recent study we demonstrated that CO has a mitigating effect on carbon corrosion in HT-PEFCs during simulated start/stop cycling. In this study we extend our investigations regarding this phenomenon. At first, a parameter study was carried out in which the temperature, the water partial pressure, the gas flow rate and the CO partial pressure were varied and their individual influence on carbon corrosion examined. Subsequently, a detailed comparison between start/stop cycling with and without CO in the fuel gas was performed (rapid aging study). This comparison includes real-time carbon corrosion detection via a CO2 sensor and current mapping in 100 segments. In addition, the electrochemically active surface area (ECSA) was measured in spatially resolved manner alongside polarization curves, characterizing the fuel cell prior and after the simulated start/stop cycling. The results show how CO is mitigating the degradation of the HT-PEFC cathode on a local level. Moreover it was demonstrated that CO in the anodic fuel gas can increase the life-time of HT-PEFCs.

The HT-PEFCs top argument in the ongoing global quest for establishing alternative and renewable energy supplies is its ability to tolerate diluted or impure hydrogen as fuel gas. Depending on operating temperature, CO hardly affects fuel cell performance up to a concentration of approximately 3%.1,2,18 LT-PEFCs, in comparison, are only capable to tolerate a significantly smaller CO concentration of around 10 ppm.1 Nevertheless, notwithstanding other positive aspects, such as the possibility to use dry reactants, PEFCs (LT as well as HT) suffer from start/stop induced carbon corrosion. During start-up or shut-down of a PEFC a fuel/air gas front propagates through the fuel electrode (anode) compartment. This transient gas front causes high potentials (up to 1.5 V)1,3 on the air electrode (cathode). Carbon is already beyond its thermodynamic stability (cf. Equation 1, $E^\circ = 0.207\ V$ versus SHE) on the air electrode under steady-state conditions. But due to the sluggish reaction rate at 1 V the corrosion rate is rather slow. The high potential peaks during start/stop, in contrast, are very much relevant and lead, besides catalyst particle growth and platinum dissolution, to rapid and irreversible carbon corrosion. For a detailed introduction to the start/stop- or reverse current decay-mechanism the reader is referred to previous literature.4,6–10

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad E^\circ = 0.207\ V \text{ versus SHE} \quad [1]$$

Carbon corrosion drastically reduces fuel cell performance and life-time as a result of catalyst particle detachment and particularly loss in mechanical electrode integrity. Therefore, in order to reach the designated life-time of 60,000 to 80,000 hours until 202011 it is indispensable to find reliable, efficient and effective methods to suppress carbon corrosion caused by fuel cell start-ups or shut-downs. There are a vast number of publications and patents, for HT- as well as for LT-PEFCs, which tackle this very problem. In general, the approaches can be categorized into material and operation based mitigation strategies. From a materials perspective the research focus is on stabilized graphitized carbon1,12–15 or carbon free (metal oxides)12–15 catalyst supports. Recently, among others,16,17 also nanostructured thin films have gained attention as possible corrosion resistant alternative catalyst layer architecture.18 Those strategies are very promising for future applications. Common mitigation strategies on the operation level are high flow rates (purging)19,20 and auxiliary loads.11,12 Both methods are effective and can be implemented in a straightforward manner, especially the purging when a respective inert purge gas can be used in a fuel cell system installation. We recently proposed an additional way to reduce carbon corrosion, which to the best of our knowledge has not been considered so far. With an increasing partial pressure of CO in the fuel gas, the carbon corrosion rate at the air electrode is considerably reduced.20 In the present study we expanded our investigations to gain more insight into this mitigation strategy.

At first, a broad parameter study was performed, in which the cell temperature, the gas flow rate and the water and CO partial pressures, respectively, were varied to examine their individual influence on carbon corrosion. Subsequently, a detailed comparison was focused on the influence of CO by characterizing performance and electrochemical surface area (ECSA) of a fuel cell, prior to and after cycling it without and with 10 vol% CO for 50 start-ups and 50 shut-downs (rapid aging study). In addition, through current mapping in 100 segments, a spatially resolved analysis of the effect of CO is performed.

**Experimental**

For all experiments a BASF Celtec based membrane electrode assembly (MEA) was used. The MEAs exhibit a thickness of approximately 820 μm including a membrane thickness of around 50–75 μm. The MEA consists of a highly H3PO4 doped polybenzimidazole (PBI) membrane, electrodes with a platinum loading of 1 mgPt cm−2 on anode and cathode, respectively, an active area of 45.15 cm2 and a carbon paper gas diffusion layer. During break-in (50 h at 0.2 A cm−2 and 2.0 for air. Furthermore, from here on the electrode normally operated as fuel cell anode is referred to as the fuel electrode, whereas the electrode normally operated as fuel cell cathode is denoted as air electrode.26 The start/stop events were performed by switching the fuel electrode gas feed every 180 seconds (one complete cycle in 360 s) from a fuel gas composition to synthetic air and vice versa. At the air electrode synthetic air is used throughout the experiment. Please note that in our previous publication pure oxygen was used as oxidant.25 Two three-way magnetic valves (Bürkert Type 0330) are used for switching the fuel electrode gas supply intermittently. During the start/stop cycling the cell was at open circuit voltage. For detecting the carbon corrosion a real-time infrared based CO2 sensor was used (California Analytical Instruments Model 601) with a detection range up to 1000 ppm CO2. The exhaust gas stream from the air electrode is fed through a cold trap to condense water before being sent to the CO2 sensor to avoid interference of the measurement by residual humidity. The amount of corroded carbon $n_{cc}$, measured via the CO2 sensor, was calculated according to

$$n_{cc} = M_C \cdot n_{CO_2} = M_C \cdot \frac{pV}{RT} \cdot \Delta CO_2\text{--Peak} \quad [2]$$
where $A_{CO_2-peak}$ is the area of the CO$_2$ peak (ppm·s) measured by the infrared sensor at the exhaust of the air electrode. $R$ is the universal gas constant, $p$ and $T$ are the ambient pressure and temperature, respectively, $M_C$ is the molar mass of carbon, and $\dot{V}$ is the effective volumetric gas flow rate. At least two CO$_2$ start-up/shut-down peaks were used to average $m_{cc}$.

For the parameter study, three different fuel flow rates (12, 18 and 24 Nl/h$^{-1}$ corresponding to residence times of 1.30, 0.87 and 0.65 s), cell temperatures (80, 120 and 160 $^\circ$C), and CO concentrations (0, 5 and 10 vol%) were applied. In addition, the gases on the fuel electrode were humidified at room temperature (corresponding to a water partial pressure of ca. 31.7 mbar) for one complete set of parameters, and non-humidified for another set of parameters.

For the rapid aging experiments the hydrogen concentration in the fuel gas was kept constant at 90 vol%, and 10% N$_2$ or CO was used in case of cycling in the absence or presence of CO, respectively. All other parameters are kept unchanged to focus on the influence of the presence of CO. The fuel cell temperature was 160 $^\circ$C and the gas flow rate was set to 12 Nl/h$^{-1}$ on both electrodes. This flow rate corresponds to a gas front residence time of 1.30 s in the flow field. The flow field has meandering channels and the gas inlet and outlet position is identical for both electrodes (co-flow). Prior to and after 100 cycles (50 shut-downs and 50 start-ups) the ECSA was measured and a polarization curve was recorded. The ECSA was determined by the reference cycle technique introduced in Ref. 27. The polarization curves were measured with pure hydrogen ($\lambda = 1.2$) and air ($\lambda = 2.0$). Those experiments are supported by spatially resolved current measurements via a 10 by 10 shunt resistor matrix (for details see Ref. 27). Hence, a thinner flow field (4 mm) was used compared to the parameter study (10 mm) to reduce leak currents. This matrix is also used to calculate the amount of corroded carbon on a local scale, which is explained in more detail later on.

Results

Parameter study.— This study was made to improve the understanding of the influence of different cell operating parameters on carbon corrosion at the air electrode of a HT-PEFC with special attention to the presence of CO in the fuel gas. The result for the first set of parameters (no humidification) is presented in Figure 1. Obviously, the temperature has the strongest effect on the amount of corroded carbon for start-ups as well as for shut-downs. Also, higher flow rates lead consistently to reduced corrosion. An increased CO partial pressure ($p_{CO}$) suppresses the carbon oxidation at start-up (Figure 1a) and shut-down (Figure 1b), whereas the mitigation is more pronounced for the latter situation. At 120 $^\circ$C and only 5 vol% of CO, there is 10 times less carbon corrosion detectable compared to 0 vol% of CO, which is quite remarkable.
Figure 2. Amount of corroded carbon $m_{cc}$ during start-up a) and shut-down b) as a function of temperature $\theta$, flow rate $\dot{V}$ and CO partial pressure $p_{CO}$. The fuel electrode gas feed (H2/CO or synthetic air) was fully humidified at room temperature.

Comparison start/stop cycling with and without 10% CO – rapid aging study.— We have shown that the presence of CO does reduce carbon corrosion within a broad parameter range, especially in case of shut-downs. This is a needed but not necessarily sufficient requirement for improving the life-time of HT-PEFCs. Therefore, the question remains if CO is able to increase the life-time of HT-PEFCs. This question will be addressed in the following by 100 start/stop cycles in a rapid aging test.

Two MEAs were conditioned identically and characterized prior to the aging test. Subsequently, both cells were shut-down 50 times and also started for 50 times by switching the fuel electrode gas stream. The hydrogen partial pressure was kept at a constant 90 vol%, the remaining 10 vol% consisted of N2 or CO, depending on the experiment.

Once more, the mitigation effect of CO is demonstrated in Figure 3. Figure 3a highlights the raw data of the CO2 sensors at the exhaust of the air electrode for one start-up and one shut-down event at the beginning of test (BOT) and end of test (EOT) in the absence of CO. Figure 3b indicates the corresponding data for cycling in the presence of CO. The CO2 concentration is again consistently lower in the latter case, at start-up and shut-down as well as at BOT and EOT. The peak
The integration over all 100 cycles leads to the results presented in Figure 4. In combination, for start and stop events the presence of 10 vol% CO in the fuel gas reduces the amount of oxidized carbon by approximately 30%. For shut-downs it is even 64%.

In the experimental setup used here, carbon corrosion is not only quantified via a CO2 sensor in the air exhaust, but additionally determined spatially resolved in a semi-quantitative manner via the introduced segmented resistor matrix. It is semi-quantitative because not all electrons will pass the matrix during start-up and shut-down due to the finite conductivity of the flow field. Nevertheless, this effect is identical for all experiments and therefore a relative quantitative comparability is possible.

A short movie captured by the resistor matrix illustrates a gas front passing through the cell during a start-up and a shut-down transient, which can be found online (cf. supplementary information). In these movies positive currents indicate normal cell operation; negative currents are associated with reverse-current operation. The current response for five different segments is illustrated in Figure 5 for a shut-down (a) and start-up (b) event, respectively. One can clearly see that the current in the segments close to the gas inlet is mostly negative during shut-down, indicating reverse-current and thus carbon corrosion. In contrast, during start-up the segments close to the gas outlet are subject to carbon corrosion. This behavior is in excellent agreement with the theory of start/stop phenomena reported in literature.4,6

Also, the currents are higher during start-up compared to shut-down, which is again in very good agreement with the pseudo-capacitive effect mentioned earlier. The current oscillation in Figure 5b can be attributed to the resistor matrix limited sampling rate (approximately 100 ms). For more detailed insights, all negative currents per
Figure 6. Estimate of spatially resolved carbon corrosion for one shut-down without CO (a) and with 10 vol% CO (b).

Figure 7. Spatially resolved carbon corrosion for one start-up without CO (a) and with 10 vol% CO (b).

segment were integrated via Equation 3 to yield an estimate for the spatially resolved amount of corroded carbon during one shut-down and one start-up across the air electrode. Please note that Equation 3 is based on an ideal model where no side reactions and no leaking currents occur.

\[ m_{cc,\text{segment}} = M_C \cdot j_{\text{neg,segment}} \cdot t \cdot 4F \]  \[3\]

Here \( m_{cc,\text{segment}} \) is the amount of corroded carbon per matrix segment, \( M_C \) is the molar mass of carbon, \( j_{\text{neg,segment}} \) is the negative current transient during one start or stop event per segment, \( t \) is the time in which one of those event occurs, and \( F \) is the Faraday constant. Furthermore, a factor of four is included because it takes four electrons to oxidize one carbon atom (cf. Equation 1). It is also important to note that the amount of corroded carbon calculated by the integration of the negative currents can only be a relative quantitative estimate due to side reactions which occur during a shut-down/start-up,\(^{29-31}\) and also due to the high flow field conductivity as mentioned above. Nevertheless, with this approach it is still possible to highlight the influence of CO regarding its ability to suppress carbon oxidation because those side effects are similar for all experiments.

The observation made earlier in Figure 5 is even more apparent after the current integration. A stop-event causes carbon oxidation almost exclusively in the electrode area close to the gas inlet. More importantly, the difference in corroded carbon per segment between a shut-down with (a) and without (b) CO is remarkable (cf. Figure 6). A corrosion drop by roughly two-third is very promising and furthermore correlating very well with the integral results obtained via the CO\(_2\) sensor. In comparison, the carbon corrosion during a start-up follows an opposite trend, it occurs mainly in the electrode area close to the gas outlet (cf. Figure 7). The local resolution confirms furthermore that the benefit of CO is less pronounced during a cell start. Subtracting the results from the cycling with (Figure 6b and Figure 7b) and without CO (Figure 6a and Figure 7a) separately highlights the benefit of CO for a shut-down and start-up (not shown here).

By subsequently summarizing those values the overall amount of ‘saved’ carbon for one start-up and one shut-down is illustrated in Figure 8. It is important to keep in mind that the mitigating effect is most pronounced in the area closer to the gas inlet.

The effect of CO regarding its ability to mitigate carbon corrosion was characterized in detail. Nevertheless, its effect on the conservation of ECSA and performance after 100 start/stop cycles remains unknown thus far and will therefore be evaluated in the subsequent section.

The ECSA was measured before and after the cycling via the reference cycle routine discussed in Ref. 27. Overall, 10 vol% of CO in the fuel gas stream diminishes the ECSA loss by around 10% after 100 simulated start/stop cycles. Besides this overall result we were furthermore able to measure the decrease in ECSA in spatially resolved manner revealing compelling insights.
More precisely, measuring the ECSA globally would not highlight the local and individual difference in ECSA loss between the cycling with and without CO, which is shown in Figure 9. The maximum decrease in ECSA is observed in the regions close to the gas in- and outlet if there is no CO present during the start/stop cycling (cf. Figure 9a). Cycling with CO (cf. Figure 9b), in contrast, prevents the local ECSA degradation peak close to the gas inlet. These observations are in good agreement with the local corrosion results discussed earlier. CO in the fuel electrode gas reduces the carbon corrosion mainly during a shut-down event. In addition, the area which mainly suffers from carbon corrosion during a shut-down is close to the gas inlet. Accordingly, CO suppresses the carbon corrosion at the inlet area and therefore reduces ECSA loss in this electrode region. Therefore, we have the first indication that CO can increase the life-time of a HT-PEFC.

This claim is further supported by evaluating the polarization curves recorded before and after the start/stop cycling. In Figure 10 the current density change per segment is indicated at an average current density of 0.5 A cm\(^{-2}\). The total current obviously needs to stay the same but there is a notable change in the current distribution. The cycling without CO reveals that in those regions where the highest carbon corrosion occurs and especially the ECSA drop is most prominent (gas in- and outlet) also the local current density drop is most pronounced (Figure 10a). For the cycling with 10 vol\% CO the...
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during transient (start-up and shut-down) conditions.

Among the measured current density range CO diminishes the polari-
zation loss by approximately 10 mV. The presence of CO during start/stop cycling is therefore reducing the performance degradation and is consequently enabling longer lifetimes of HT-PEFCs under transient (start-up and shut-down) conditions.

Conclusions

In this manuscript, we have shown that CO in the fuel electrode
gas is able to decrease the amount of corroded carbon caused by the

reverse current decay phenomena during start-up and shut-down at
the air electrode in a broad parameter range (flow rate, temperature, CO partial pressure, humidity). Especially during stop events the mitigating effect is pronounced, where 10 vol% of CO in the fuel gas can suppress carbon corrosion on the air electrode by up to 85%.

Moreover, a simulated life-time study was carried out. Two sepa-
rate yet identical HT-PEFCs were started-up and shut-down for 100

start/stop cycles at 100 times by switching the fuel electrode gas supply between synthetic air and 90 vol% hydrogen. For the remaining 10 vol% CO and N2 were added in the two experiments, respectively. Both cells were compared and characterized before and after the cycling (spatially resolved) polarization curves and ECSA measurements. In addition, the amount of corroded carbon was recorded. It turns out that CO mitigates the loss in ECSA upon cycling. Furthermore, it was visualized that the mitigating effect mainly occurs in the electrode area close to the gas inlet. Most importantly, CO also decreases the performance loss, originating from the electrode degradation due to the start/stop cycling. Between OCV and 1 A cm⁻² the gain is approximately 10 mV.

Therefore, CO in the fuel gas can increase the life-time of HT-

PEFCs. It mitigates the degrading effect of start-ups and shut-downs. From a practical engineering perspective, about 10 vol% of CO is a common concentration at the exit of a reformer, prior to any addi-
tional gas treatment. Hence, increasing the CO partial pressure dur-

ing start/stop can be easily implemented by, for example, bypassing CO cleaning steps. We are convinced, therefore, that the effect can and should be enhanced by supplementary operation adjustments. Some fuel gas (including CO) should be stored in the anode compart-
ment after a shut-down and not purged out. It most certainly sustains the CO mitigating effect for the subsequent start-up to some extent. Also, comparing durability experiments with e.g. 1000 cycles should be carried out in order to establish more application-relevant con-
ditions. These and other opportunities will be featured in upcoming investigations.

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Figure 11. Potential difference of the polarization curves recorded before and after 100 start/stop cycles.