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 with 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.

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 Pt/Pd doped polybenzimidazole (PBI) membrane, electrodes with a platinum loading of 1 mgPtcm⁻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 Acm⁻² and 2.0 for air) the MEC was operated at stoichiometries of 1.2 for hydrogen and 2.0 for air. Furthermore, from here on the electrode normally operated as fuel cell cathode is denoted as air electrode and 2.0 for air. The MEA consists of a highly Pt/Pd doped polybenzimidazole (PBI) membrane, electrodes with a platinum loading of 1 mgPtcm⁻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 Acm⁻² and 2.0 for air) the MEC was operated at stoichiometries of 1.2 for hydrogen and 2.0 for air. Furthermore, from here on the electrode normally operated as fuel cell cathode is denoted as air electrode.

The start/stop events were performed by 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 10'000 ppm CO₂. The exhaust gas stream from the anode was fed through a cold trap to condense water before being sent to the CO₂ sensor. The exhaust gas stream from the anode was fed through a cold trap to condense water before being sent to the CO₂ sensor (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 Pt/Pd doped polybenzimidazole (PBI) membrane, electrodes with a platinum loading of 1 mgPtcm⁻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 Acm⁻² and 2.0 for air) all cells were operated at stoichiometries of 1.2 for hydrogen and 2.0 for air. Furthermore, from here on the electrode normally operated as fuel cell cathode is denoted as air electrode.

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. 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 10'000 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_C, measured via the CO₂ sensor, was calculated according to

\[ n_C = M_C \cdot n_{CO_2} = M_C \cdot \frac{P \cdot V}{RT} \cdot \Delta CO_2 \text{--Peak} \]
where $A_{CO_2}$ 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 $V$ 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 Nlh$^{-1}$ corresponding to residence times of 1.30, 0.87 and 0.65 s), cell temperatures (80, 120 and 160°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°C and the gas flow rate was set to 12 Nlh$^{-1}$ 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°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.
The results with fuel gas streams humidified at room temperature in Figure 2 are qualitatively very similar to those without humidification. Nevertheless, the carbon oxidation is overall more pronounced during start-ups if there is water present in the gas stream. For shut-downs, the effect is less noticeable. Again, the temperature is crucial for start-ups and shut-downs as well as the flow rates. Increasing the CO partial pressure also reduces carbon corrosion considerably, especially during shut-down.

Higher reaction kinetics are favored by elevated temperatures. Therefore, the carbon oxidation is more pronounced at 160°C compared to 80°C. In addition, the membrane proton conductivity also increases with higher temperatures. Hence, the reverse current mechanism might be additionally promoted. An increase in carbon corrosion with decreasing flow rates is also reasonable and well in agreement with experiments reported in literature for LT-PEFC.28 The gas front residence time in the flow channel increases with smaller flow rates. Thus, the reverse current situation is prolonged, leading to higher carbon oxidation values. The mitigating effect of CO is already described in our previous publication.25 In short, CO adsorbs on the fuel electrode, suppressing the ability to oxidize hydrogen/reduce oxygen during the gas exchange process. Therefore, carbon oxidation at the air electrode is limited.

In summary, the highest mitigation effect is achieved with high flow rates, low temperatures and high CO partial pressures for shut-downs and start-ups, regardless if humidified or dry fuel gases are used.

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
difference between the start-up and the shut-down in Figure 3a (no CO) is related to pseudo-capacitive effect, which is well known in literature.4,6–10

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).

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.
Figure 8. Spatially resolved reduction of carbon corrosion (‘saved carbon’) due to 10 vol% of CO in the fuel gas stream during one start-up and shut-down.

Figure 9. Spatially resolved decrease in ECSA after 100 start/stop cycles with (a) and without (b) CO.

Figure 10. Spatially resolved change in current density after 100 start/stop cycles with (a) and without (b) CO at 0.5 A*cm$^{-2}$.

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
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 compartment 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 conditions. These and other opportunities will be featured in upcoming investigations.

Acknowledgments

Financial support from BASF SE is gratefully acknowledged. We thank our colleagues at PSI for technical assistance and productive discussions.

References

1. T. J. Schmidt and J. Baumeister, Durability and Reliability in High-Temperature Reformed Hydrogen PEFCs, in: ECS Transactions, 3, 861 ECS (2006).
2. Q. Li, R. D. He, J. O. Jensen, and N. J. Bjerrum, Fuel Cells, 4, 147 (2004).
3. A. D. Modestov, M. R. Tarasevich, V. Y. Filimonov, and E. S. Davydova, Electrochim. Acta, 55, 6073 (2010).
4. C. A. Reiser, L. Bregoli, T. W. Patterson, J. S. Yi, J. D. Yang, M. L. Perry, and T. D. Jarvi, Electrochim. Solid-State Lett., 8, A273-A276 (2005).
5. T. J. Schmidt, High-Temperature Polymer Electrolyte Fuel Cells: Durability Insights, in: F. N. Büchi, M. Inaba, and T. J. Schmidt, Editors Polymer Electrolyte Fuel Cell Durability, pp. 199–221, Springer New York, New York (2009).
6. W. Gu, R. N. Carter, P. T. Yu, and H. A. Gasteiger, ECS Trans., 11, 963 (2007).
7. C. Hartung and T. J. Schmidt, J. Power Sources, 196, 5564 (2011).
8. W. Gu, P. T. Yu, R. N. Carter, R. Makharia, and H. A. Gasteiger, Modeling of Membrane-Electrode-Assembly Degradation in Proton-Exchange-Membrane Fuel Cells – Local H2 Starvation and Start-Stop Induced Carbon-Support Corrosion, in: F. Y. Wang and U. Pasaogullari, Editors Modeling and Diagnostics of Polymer Electrolyte Fuel Cells Modern Aspects of Electrochemistry, pp. 45–87, Springer New York, New York (2010).
9. S. Kreitmeier, A. Wokaun, and F. N. Büchi, J. Electrochem. Soc., 159, F787 (2012).
10. A. P. Young, V. Colbow, D. Harvey, E. Rogers, and S. Wessel, J. Electrochem. Soc., 160, F381 (2013).
11. U.S. Department Of Energy, Fuel Cell Technologies Office: Multi-Year Research, Development, and Demonstration Plan - 5.4 Fuel Cells, (2013).
12. E. Antolini and E. R. Gonzalez, Solid State Ionics, 180, 746 (2009).
13. T. Binninger, E. Fabbri, R. Koezt, and T. J. Schmidt, ECS Trans., 58, 1835 (2013).
14. E. Fabbri, A. Paltur, A. Rabis, R. Kötz, and T. J. Schmidt, Chimia (Aarau), 68, 217 (2014).
15. E. Fabbri, A. Rabis, R. Kötz, and T. J. Schmidt, Phys. Chem. Chem. Phys., 16, 13672 (2014).
16. B. Genorio, D. Strmenic, R. Subbaruman, D. Trpkovic, G. Karapetrov, V. R. Stamenkovic, S. Pejovnik, and N. M. Markovic, Nat. Mater., 9, 998 (2010).
17. L. Liu, P. Rodriguez, L. Borchart, A. Foelske, J. Yuan, A.-K. Herrmann, D. Geiger, Z. Zheng, S. Kasel, N. Gaponik, R. Kötz, T. J. Schmidt, and A. Eychmüller, Angew. Chem. Int. Ed. Engl., 52, 9849 (2013).
18. M. K. Debe, Nature, 486, 43 (2012).
19. A. C. Reiser, J. D. Yang, and R. D. Sawyer, US Patent 2002/0076583 A1, 20 Jun 2002 (2002).
20. R. J. Balliet, C. A. Reiser, T. W. Patterson, and M. L. Perry, US Patent 2004/0126628 A1, 1 Jul 2004 (2004).
21. P. T. Yu, US Patent 2006/0040150 A1, 3 Feb 2006 (2006).
22. L. Van Dine, M. M. Steinbügl, C. A. Reiser, and G. W. Scheﬄer, US Patent 2002/0098393 A1, 25 Jul 2002 (2002).
23. R. J. Balliet and C. A. Reiser, US Patent 2004/0001980 A1, 1 Jan 2004 (2004).
24. T. A. Bekkedal and R. D. Breault, US Patent 2004/0081866 A1, 29 Apr 2004 (2004).
25. T. Engl, J. Käse, L. Gubler, and T. J. Schmidt, ECS Electrochem. Lett., 3, F47 (2014).
26. M. L. Perry, R. M. Darling, S. Kandori, T. W. Patterson, and C. A. Reiser, Stack Durability Operating Requirements for Durable Polymer-Electrolyte Fuel Cell Stacks, in: F. N. Büchi, M. Inaba, and T. J. Schmidt, Editors Polymer Electrolyte Fuel Cell Durability, pp. 399–417. Springer New York, New York (2009).
27. T. Engl, K. E. Walter, L. Gubler, and T. J. Schmidt, J. Electrochem. Soc., 161, F500 (2014).
28. N. Linse, G. G. Scherer, A. Wokaun, and L. Gubler, J. Power Sources, 219, 240 (2012).
29. J. Dillet, D. Sperrjakt, A. Lamibrag, G. Maranzana, R. Mukundan, J. Fairweather, S. Didierjean, A. R. Borup, and O. Lottin, J. Power Sources, 250, 68 (2014).
30. J. P. Meyers and R. M. Darling, J. Electrochem. Soc., 153, A1432 (2006).
31. P. Tu, W. Gu, R. Makharia, T. W. Wagner, and H. A. Gasteiger, ECS Trans., 3, 797 (2006).