Solid oxide fuel cells are high-efficient devices, which convert the chemical energy of gaseous fuels directly into electrical energy without additional conversion steps. The heat losses occurring during the operation at temperatures between 600–1000°C can be used as a high-quality heat energy. SOFCs offer a great fuel flexibility and compared to other fuel cell types they can internally reform hydrocarbons. Internal conversion of carbon-containing fuels over nickel as the most widely used catalyst tends to promote carboneous deposits on the anode surface as well as inside the anode, causing deactivation of the fuel cells.\textsuperscript{1–4} The usage of other alternative materials such as Cu-, Gd- and Sm-stabilized ceria-based materials or conducting oxides is possible to suppress carbon depositions, but Ni still offers a considerably better conductivity and electrocatalytic performance.\textsuperscript{5–7}

**Carbon deposition.** To date many researchers have investigated SOFC anode degradation. Khan et al.\textsuperscript{5} made a short review of Ni-YSZ degradation mechanisms, classifying these into four types: nickel coarsening, coking, redox instability and sulfur poisoning. A detailed analysis of challenges for nickel steam-reforming catalyst for industrial application can further be found in study from Sehestad.\textsuperscript{9} However, regarding operation of Ni-YSZ based SOFCs, if the cell is operated under expected conditions, which exclude sulfur in the fuel and the presence of oxygen on the anode side, redox instability and sulfur poisoning can be excluded as possible degradation phenomena. Nickel coarsening is a process where metal powder begins to sinter and small particles grow in size. It reduces the cell conductivity and worsens the cell performance. The sintering of nickel is also known to prone carbon formation, which requires prevention of this mechanism in order to reduce carbon build.\textsuperscript{9} Coking can lead to an irreversible change of the cell microstructure and cause mechanical degradation, which both lead to a performance degradation.\textsuperscript{10} Deposited carbon can block the pores in the fuel electrode and block the gas transport in the porous anode. Furthermore, the nickel-catalyst and three-phase-boundary can be covered and for this reason the chemical and electrochemical reactions, as well as current generation, can be inhibited.\textsuperscript{11} Many researchers have investigated the impact of different fuels with carbon contents, both experimentally and numerically, and demonstrated their degrading effect on the cell performance and the cell microstructure.\textsuperscript{3,11–19} Based on 17,18,20–22 operating temperature defines the structure of the carbon formed. High operating temperatures (higher than 600°C) intensify methane cracking, while the possibility of carbon formation by the Boudouard reaction is increased at lower temperatures, especially at temperatures lower than 600°C. Risk of carbon formation and deposition on industrially-relevant Ni-catalyst during steam- and dry-methane reforming, types of carbon formed as well as occurring reaction mechanisms are carefully analyzed by Haldor Topsoe. For detailed information readers are referred to 3–27. Snoeck et al.\textsuperscript{28} claim that the Boudouard reaction results in the formation of encapsulating carbon, which induces the gradual catalyst deactivation. Encapsulated carbon through methane cracking was formed only at lower partial pressure of methane and in the absence of hydrogen. Filamentous carbon was formed mainly during the normal methane operation. Chen et al.\textsuperscript{29} verified experimentally that the increased volume fraction of methane and decreased volume fraction of hydrogen and carbon monoxide in a gas mixture drastically changed the anode morphology and deteriorated the cell performance. The impact of methane and carbon monoxide on the type of carbon formed and its morphology was reported also by Xiao et al.\textsuperscript{4} They claimed that carbon formed through methane cracking cannot destruct the anode structure and the amount of carbon formed increased with increasing temperature, while the carbon formation due to carbon monoxide decreased with an increasing temperature.

**Carbon removal.** An important goal in order to prolong the lifetime of SOFCs is not only to avoid the formation of carbon, but to develop cell-protecting carbon removal strategies. This topic needs to be scrutinized, due to insufficient attention having been paid to it so far in the scientific community. Kirtley et al.\textsuperscript{31} employed in situ vibrational Raman spectroscopy in order to examine the rates of carbon
deposits over the Ni/YSZ anode, and furthermore to detect the rates of carbon removal and Ni-oxidation. In their study, \( H_2O, CO_2 \) and \( O_2 \) were used as reforming agents. Ni-oxidation was detected independent of the component used, when the anode was supplied with the specific gasification agent further after carbon was removed. This implicates the need for continuous control of the carbon gasification and the ensuring the undisturbed anode supply. This study demonstrated in any case that hydrogen, steam or carbon dioxide may gasify any carbon formed due to different reactions. Snoek et al.\textsuperscript{20} also studied carbon gasification by using \( CO_2 \), \( H_2 \) and steam, and showed a modeled and experimentally observed gasification rate. In their study, the gasification process was performed at 550 °C and it was shown that carbon gasification can differ depending on that whether the carbon is formed by methane cracking or the Boudouard reaction. Furthermore, the catalytic activity of various Ni-based catalysts for methane conversion and carbon re-gasification by \( CO_2 \) was examined by Take-naka et al.\textsuperscript{22,32,33} They investigated the structural changes of Ni species influenced by the carbon depositions and their removal. It was also shown that catalytic activity and microstructure of Ni changed after every newly performed methane decomposition - gasification with \( CO_2 \) cycle. Detailed analysis of the cell microstructure after repeating the coking and coke-removal processes was also shown by numerous SEM-images and XRD-patterns. A very interesting fact shown in their study is that the size of the carbon nanofibers formed is dependent on the dimensions of the Ni-particles. However, all these researchers showed that carbon gasification by carbon-dioxide is possible. Nevertheless, the performances of solid oxide fuel cells after the removal of carbon are not investigated and it is not known, if the initial SOFC electrochemical performance could still be achieved. In our presented study, in order to enable a continued and efficient cell operation, the aim is not only to remove the carbon that has been formed, but also to restore the cell performance without degrading the cell microstructure.

**Objective of this study.**—The present study is focused on experimentally investigation of two major points, which impact a safe operation of SOFC-systems: carbon deposition and carbon removal. Firstly, guidance about the problematic issue of carbonaceous deposits on the anode-supported solid oxide fuel cells is provided. For the safe operation of SOFC-systems and APU-units it is necessary to determine an impact of carbon depositions on the anode-stability and its microstructure. We thus generated conditions under which carbon will build up and generally scrutinized its impact on the electrochemical, mechanical and morphological cell properties. For this purpose, the amount of methane in the diesel reformate, used as a fuel mixture is varied, since most carbon is formed in methane at SOFC operating temperatures. The experimental study proves that carbon depositions worsen the steam- and dry-reforming and generally downgrade the electrochemical performance. Furthermore, this study demonstrates that carbon induces a degradation of the lattice cell microstructure causing a crushing of yttria-stabilized-zirconia particles and their deposition on the Ni-catalyst. By this means a complete change is achieved in the overall microstructure and electrochemical properties. The degradation effect referred to is of significant importance in order to correctly detect the in-operando electrochemical performance alternation that occurs. The proper identification of this degradation phenomenon ensures the safe operation of SOFC systems and enables consideration of this additional effect during an in-operando characterization of the processes taking place. Secondly, this study investigates the potential for using carbon dioxide as carbon gasification agent in SOFC systems. This investigation is of key importance to prolong the lifetime of SOFC cells and to accelerate the commercialization of SOFC-systems. In order to obtain information about the possibility for fast carbon removal without changing the operating conditions, all investigations regarding usage of carbon dioxide are performed at 800 °C, which is defined as optimal operating temperature, as specified by the manufacturer of the anode-supported single-cells used. An additional reason for this is to prevent the fast Ni-oxidation on the fuel electrode. The oxidation potential, depending on the gasification by carbon-dioxide, is investigated numerically by our group and is described in ’CFD-Simulation of Effective Carbon Gasification Strategies From High Temperature SOFC Ni-YSZ Cermet Anodes’. Therein it is shown that a temperature decrease from 800 °C to lower temperatures significantly increases oxygen coverages on the anode. Therefore, no thermal cycling is performed and the aim is to investigate and to develop possible regeneration strategies without varying the operating temperature. Several cells were used for investigation of every single gasification method, which was repeatedly carried out for each cell, to ensure reproducibility. During the gasification process with \( CO_2 \) carbon-monoxide was measured at the anode outlet. Nevertheless, this method for carbon gasification did not prove successful and further performance degradation occurred. The same effect of this regeneration strategy, based on CFD-simulation, is also represented and described in our numerical study, already mentioned above. In our previous study\textsuperscript{34} we showed that carbon formed in synthetic diesel reformate can be removed in cell-protecting way by using a gas mixture hydrogen/steam/nitrogen. The strategy applied provided carbon removal and restored the initial cell performance. In order to enable cell-protecting carbon removal without further deterioration of the cell performance by using \( CO_2 \), we examined a new strategy. The anode was supplied with \( CO_2 \) for the purpose of carbon gasification and a protecting overvoltage was set during the gasification process to prevent cell performance deterioration. To the best of our knowledge, carbon dioxide in combination with protecting overvoltage has never been used for the purpose of carbon removal and the regeneration of the cell performance of solid oxide fuel cell. It is also of significant importance for the applied carbon removal principle that investigated anode-supported SOFC cells are of industrial-size, which is relevant for commercial usage. The investigation of such large cells is far more complex compared to cells with a small active area, since fuel utilization and temperature, as well as many other parameters differ greatly with the cell dimension.

**Experimental**

**Cell geometry.**—Anode supported SOFCs single cells with a porous Ni/YSZ anode and a LSCF-cathode were tested in this study. The geometrically active area of the cells investigated was 81 cm\(^2\). The anode substrate was fabricated with an average thickness between 200–300 \( \mu m \) and a 10 \( \mu m \) thick Ni/\( \text{ZrO}_2 \) anode functional layer was added onto it. The YSZ-electrolyte had the same thickness of approximately 10 \( \mu m \). A 5 \( \mu m \) thick CeO\(_2\) barrier layer and the lanthanum strontium cobalt ferrite (LSCF) cathode with a thickness of around 30 \( \mu m \) were added onto the electrolyte. The geometry of the layers in the cell is shown in Fig. 1.

**Experimental setup and testing procedure.**—SOFC cells were placed in a ceramic single cell housing that was embedded in a temperature-programmed furnace. Nickel meshes were used as current collectors for fuel electrode, whereas platinum meshes were used to contact the air electrode. The cathode side was fueled with synthetic air. Different fuel mixtures were fed to the anode in co-flow condition, according to the values showed in Table I. The exact volume flow of every individual gas component (hydrogen, nitrogen, carbon monoxide, carbon dioxide, methane, synthetic air) was defined using mass flow controllers. If requested, the fuel used was humidified in a humidifier unit. Temperature was measured at several points on the anode surface, at the anode-inlet and anode-outlet as well as in the furnace. The operating temperature was maintained constant at 800 °C. During the experiment a gas analyzer was used to measure the concentration of single components at the anode inlet and outlet, respectively. Electrochemical measurements were performed by an electronic load and an impedance analyzer with a ±40 A booster. The measurements were performed at open circuit voltage and under load — mainly over the whole effective load range of 40 A in a frequency range from 10 kHz down to 100 mHz. An extensive and comprehensive description of the experimental setup can be found in\textsuperscript{34,35} The anode was fed with diesel reformat (DR) with varying volume fraction of methane (see Table 1). The methane in the synthetically
produced diesel reformate was added extra in order to investigate its impact on the coking and degradation rate.

**Microstructure examination.—** The scanning electron microscopy method was performed in order to analyze the microscopic topologies of the cells. Microscopic cell examination was carried out using a Zeiss Ultra 55 field emission scanning electron microscope equipped with an energy dispersive X-ray spectrometer.

**Results and Discussion**

**Detection of carbon deposition and its effect on the cell performance and microstructure.**—Synthetic reformate with compositions as expected in auxiliary power units fueled with diesel and modified diesel reformates were used to supply the tested solid oxide fuel cells. In order to obtain information about the cell performance degradation, such as critical operating time or degradation voltage, the methane volume fraction in the fuel mixture used was varied between 2.3 vol% (as expected in APUs), 9 vol% and 14 vol%, see Table I. The measured composition of gas components at the anode outlet is shown in Table II. The choice to vary the amount of methane was made, because methane cracking is favored at high operating temperatures, whilst carbon formation by Boudouard-reaction is not expected to be prominent at the operating temperature referred to. The impact of carbon monoxide and hydrocarbons on carbon formation is thus variable and does not represent a linear function of the gas concentration.

In Fig. 2 the impact of methane in the fuel mixture on the cell performance degradation. The variation of the methane amount does not mean an alternation of one single variable only, but the variation of several parameters simultaneously such as steam-to-carbon ratio or CH4/CO-ratio. The estimated time for carbon deposition is thus variable and does not represent a linear function of the gas concentration.

The operating time after which degradation of the cell performance was obvious varies between 44 hours for operation under 2.3 vol% CH4 in diesel mixture and 3 hours, if the amount of methane is increased up to 14 vol%. A decisive criterion for the determination of the elapsed time was the achievement of the stationary state. The carbon deposition experiment was performed under load to simulate more realistic operating conditions, as required for operation of APUs. During the carbon buildup current density was held as constant and the voltage was measured. The measured degradation voltage, which is calculated as the difference between the initial voltage and the voltage measured after the elapsed time, is represented in Fig. 2a. As can be seen in this figure, if the cell is operated under modified diesel reformate including 9 vol% of CH4, the voltage degradation rate of about 20 mV/h is obtained. After this period, a degradation rate is reduced down to 5 mV/h until no further degradation could be observed anymore. It could be assumed that after this period an equilibrium with carbon was reached and the amount of carbon formed equaled the amount of gasified carbon. This state is reached after 3 hours, if the cell is fueled with the mentioned fuel mixture including 14 vol% of CH4. If SOFCs were supplied with diesel reformate including 2.3 vol% of methane, no considerable impact on the cell performance was obtained until 44 hours. The degradation voltage rate over time for this case is thus not shown in the diagram in Fig. 2a.

In Fig. 2b degradation voltage is shown as function of current density. An increasing amount of methane in the fuel mixture is represented by the rising intensity of the gray color, from light gray (2.3 vol%) to black (14 vol%). The degradation voltage rate increases with increasing load, as expected, since the same degradation behavior is obtained even with pure hydrogen fuel. This effect occurs because carbon deposited on the anode surface and in the porous structure, respectively, blocks the gas channels and the three phase boundary. Therefore, the fuel supply as well as transport of oxygen ions through the anode are restricted thus increasing the overall resistance. As result of it, electrochemical reactions are reduced with the increasing current density. Furthermore, if the cell is operated with the lowest amount of carbon, whereas the most carbon is formed during the operation with methane. In principle, prediction of carbon formation under specific operating conditions is possible by thermodynamic study based on equilibrium calculations and C-H-O ternary diagram. Chemical or thermodynamic equilibrium can be used, nevertheless, for this purpose only at fast reactions and high reaction rates, respectively. The calculation of the thermodynamic equilibrium is thus insufficient for complete and meaningful description of carbon deposition phenomenon in porous SOFC’s anode substrate. Therefore, kinetics must be considered to explain the carbon deposition and possible carbon suppression mechanisms as exactly as possible. Laosiripojana et al.38 also indicated that kinetics are more important for carbon suppression than thermodynamic. For more in-depth understanding of Ni-based anodes operating under methane and other carbon-containing fuels readers are referred to comprehensive review of Wang et al.39 and studies from Tavares et al.40,41 In the present experimental study it is shown that the amount of methane in the fuel mixture has a significant impact on the carbon formation acceleration.

Table II. Volume fraction of single gas components at the anode outlet.

| Anode outlet | H2 vol% | CO vol% | CO2 vol% | CH4 vol% | H2O vol% | N2 vol% | S/C | CH4/CO |
|--------------|---------|---------|----------|----------|----------|---------|-----|--------|
| DR2.3        | 18.69   | 15.84   | 8.37     | 0.18     |          |         |     |        |
| DR9          | 32.82   | 22.84   | 5.27     | 0.31     |          |         |     |        |
| DR14         | 39.94   | 25      | 4.14     | 0.96     |          |         |     |        |

Table I. Volume fraction of single gas components at the anode inlet.

| Anode inlet | H2 vol% | CO vol% | CO2 vol% | CH4 vol% | H2O vol% | N2 vol% | S/C | CH4/CO |
|-------------|---------|---------|----------|----------|----------|---------|-----|--------|
| DR2.3       | 15.4    | 13.7    | 9.8      | 8.3      | 11       | 47.8    | 0.7 | 0.17   |
| DR9         | 15.4    | 13.7    | 9.8      | 8.3      | 11       | 47.8    | 0.7 | 0.17   |
| DR14        | 15.4    | 13.7    | 9.8      | 8.3      | 11       | 47.8    | 0.7 | 0.17   |
of methane in the gas mixture, as supposed to be in APUs, degradation voltage is detected to be between 1 mV and 8 mV in the current density range between 0 mA/cm² and 100 mA/cm², as can be seen in Fig. 2b. If more power is drawn from the cell, the degradation effect is more pronounced, as already mentioned. Such a small amount of methane caused slight deterioration of the cell performance, the maximum degradation rate at 200 mA/cm² was approximately 20 mV or 2%. The obtained degradation voltage at the same current density, for diesel reformate including 9 vol% of methane has risen as high as 80 mV which represents a degradation rate of 9%. The degradation rate increased up to 13% or 118 mV when the methane volume fraction in diesel reformate was set to 14 vol%. The same impact of methane on carbon buildup was shown by Ke et al.42 They researched the effect of the ceramic phase in Ni-supported anodes and considered that increasing operating temperature significantly increased carbon depositions on Ni-YSZ anodes, even under a certain polarization current density. The opposite trend was shown for Ni-ScSZ anodes. This effect can be explained by propensity of Ni-ScSZ anodes to adsorb H₂O onto the TPB-surface. At this point it must be mentioned that the further course of this study is based on the results obtained in experiments performed using fuel mixtures including 9 vol% and 14 vol% of methane. For more information about carbon depositions formed during operation with diesel reformate including 2.3 vol% of methane, the reader is referred to34.

The results of determining the degradation rate for the cell fueled with diesel reformate including 14 vol% CH₄ are shown in Fig. 3. The voltage and power density measured as a function of current-density for a carbon-free anode, indicated by solid black line, are compared to an anode partially covered with carbon, depicted as a dashed black line, see Fig. 3a. Significant voltage and power losses are obtained and the area between two measured curves is hatched. Coking also block active catalyst sites on the fuel electrode thus reducing the reforming activity of the cell. The loss of reforming activity can easily be detected by monitoring the methane concentration at the anode outlet. The methane volume fraction in the anode offgas, indicated by black solid line, is represented on the left ordinate in Fig. 3b, while the methane conversion rate is shown on the right ordinate as a gray solid line. During the first three hours methane volume fraction at the anode outlet increased, an overall increase of approximately 8 vol% was detected. It impacted a significant decrease of the methane conversion rate. The part of the converted methane from almost 97% was reduced for the blocked Ni-catalyst down to 40%, as outlined in Fig. 3b. Interestingly, after that the methane conversion rate remained constant until the end of the experiment. As stated above, at this state an equilibrium with carbon was reached and no additional carbon was deposited. The additional carbon deposition was therefore interrupted at this stage.

In order to detect all performance variations caused by carbon depositions, electrochemical impedance spectroscopy measurements were applied during operation on modified diesel reformate. The impedance spectra for the same fuel mixture recorded at the initial state and after 0.5 h, 1 h, 1.5 h, 4 h and 5 h are depicted in Fig. 4. The spectra are measured at current density of 120 mA/cm², in order to simulate realistic operating conditions. The beginning of the carbon buildup process on the anode surface, as shown in spectra indicated by green lines, is characterized by an improved cell conductivity and decreased overall impedance. The ability of carbon to improve the cell conductivity has also been shown in studies from Mallon and Kendall.43 They explained that small amounts of carbon link nickel
particles with each other, thus improving the anode conductivity. In this case, gas channels are not blocked and gas diffusion through the anode remains undisturbed. Eventually, additional formation and deposition of carbon leads to a coverage of the fuel supply inlet manifold, gas pores and active sites and this effect can be obtained by a rising impedance or the cell resistance, as shown with gray curve plots in Fig. 4. The impedance spectra alterations occurred in the low-frequency range refer to the anode side. In our previous study, we carried out a detailed analysis of the anode-supported SOFCs using electrochemical impedance spectroscopy. The results achieved in the mentioned study showed that variation of the operating parameters on the fuel electrode side was visible in the low-frequency range, mostly between 10 Hz and 100 mHz. The impact of the amount and position of the formed carbon on the cell performance is also proved with SEM-images.

A detailed insight in the cell microstructure before and after feeding the anode with modified diesel reformate including 9 vol% CH₄ as fuel is shown in Fig. 5. Distribution of Ni, YSZ and C particles was analyzed with EDX-mapping and accordingly to this analysis specific sites are always marked with same number: Ni (1), YSZ (2) and C (3). After the performed experiments, the Ni-YSZ surface was uniformly occupied with carbon particles and the growth of amorphous carbon on the anode surface can be seen in Fig. 5b. Kogler et al. also concluded in their experimental study that methane dissociation is possible on pure YSZ oxides, which efficiently promotes methane-induced growth of different carbon species. Amorphous carbon was identified as a dark layer without a clear structure, which covered the anode surface. Compared to this, the carbon-free Ni-YSZ anode surface is shown in Fig. 5a, where distribution of nickel and yttria-stabilized zirconia without a mixed-phase is clearly apparent. Comparison of these samples with the anode surface after carbon deposition shows strong morphological changes. Obviously, carbon deposits induced Ni-YSZ microstructure degradation, which is magnified shown in Fig. 5c. In all analyzed samples, independent of the amount of methane in the fuel stream, the presence of carbon induced the same degradation effect. The microstructural changes of Ni/YSZ are observed as crushing of YSZ-particles into very small pieces which occupied nickel particles, thus reducing the catalytic active surface. Similar degradation behavior of the Ni/YSZ-based anode structure is represented by Novosel et al. and Nikooyeh et al. Furthermore, it is apparent from the cross-section overview in Fig. 5d that carbon on the electrolyte-anode boundary layer was formed as filamentous carbon nanofibers. The morphologies visible in these figures represent reduced YSZ-particles which were not really deposited and sintered with Ni-particles, but rather exist as separated units. This carbon form indicated mechanical degradation and delamination of the electrolyte-anode boundary layer. Impact of carbon nanofibers or whisker carbon as one of the most destructive carbon forms is represented in . Rostrup-Nielsen and Trimm claimed that nickel-carbide is its preliminary stage.

### Carbon gasification by carbon dioxide

As stated in the introduction, many studies have discussed carbon gasification using carbon dioxide as a gasification agent. However, the electrochemical performance after the gasification processes cannot be found in the literature. In this part of our study, carbon removal using CO₂ as a gasification agent and its impact on the cell performance are presented. It is important to note that for this purpose CO₂ was mixed with nitrogen and hydrogen. Steam was also added to this gas mixture for further investigation. The investigations that were carried out showed that independent of the gas mixture used and the volume fraction of the single gas components, each case induced further performance deterioration. The conclusion here is that carbon dioxide has a negative impact on the cell activity. The diagrams in Fig. 6, however, only outline the measurements carried out in CO₂/N₂ gas mixture, whereby the volume fraction of CO₂ was 25 vol%, in order to make a meaningful comparison with the results shown further in this study. Carbon gasification rate for nickel foils and catalyst depending on the temperature and regarding kinetics was studied by Bernardo and Trimm. The concentration of the offgas carbon monoxide was closer to the assumed predicted concentration when the temperature increased and the flow rates decreased. The highest gasification rate was observed at higher temperatures, while at approximately 550 °C it appeared to be almost zero. During the gasification process in our study, CO-peaks were measured in the anode offgas. The greatest CO quantity of approximately 9 vol% was measured at the beginning of the gasification process and furthermore this amount decreased, as can be seen in Fig. 6a. The gasification process was completed after 3 minutes, when the CO volume fraction decreased to zero. Although it was shown by gas analysis that carbon was gasified, degradation of the cell performance occurred, as proved also by electrochemical analysis. Fig. 6b depicts the voltage and power density measured as a function of current density. Performance of a new cell, measured before the carbon deposition experiment, are indicated by black solid lines. Black dashed lines depict the deteriorated voltage and power density obtained after the cell fueling with the mentioned diesel fuel mixture, which are, as already stated, most pronounced at higher current densities. Carbon gasification using CO₂ as a gasification agent induced further cell degradation, as clearly shown by green solid lines. The voltage degradation rate that occurred, can be calculated as the
difference between the voltage obtained after the carbon deposition and after gasification with CO2. The degradation rate observed after the carbon gasification by CO2 ranges between 11 mV and 18 mV, depending on the cell load, while the maximum degradation voltage of the polarization curve measured before and after coking was 27 mV. The methane conversion rate was also significantly decreased following application of the carbon gasification strategy. CO2 thus leads to significant performance degradation and cannot be used as a cell-protecting regeneration strategy. Kirtley et al.31 observed by using carbon dioxide as gasification agent the loss of carbon and afterwards the growth of nickel oxide, which surely cause the anode degradation. Maier et al.49 developed a detailed surface reaction mechanisms in which they showed that carbon dioxide can be both adsorbed on the Ni-catalyst surface or decomposed on the anode surface. Decomposition of CO2 on the nickel surface into carbon monoxide and oxygen leads to the additional surface coverage. The observed experimental findings in this study proved the results obtained in our numerical study 'CFD-Simulation of Effective Carbon Gasification Strategies From High Temperature SOFC Ni-YSZ Cermet Anodes', which analyzes the surface conditions throughout this gasification strategy. Therein it is shown that during the gasification process, several mechanisms are responsible for further performance degradation. First, elementary oxygen can be found on the anode surface, which increases the Ni-reoxidation potential and thus can be connected to the results obtained by Kirtley et al.31 Second, carbon monoxide is adsorbed on the anode surface and the applied regeneration strategy does not reduce that adsorbed amount. Third, carbon cannot be completely removed from the anode surface, but the remaining amount of the carbonaceous species is such small that it is not possible to measure it in the experimental study. The carbonaceous species were thus not completely gasified from the active nickel catalyst, which was additionally covered with adsorbed CO and O2. This caused further performance degradation thus also disabling methane reforming and reducing the overall methane conversion rate.

Nevertheless, we combined CO2 with protective overvoltage. The value of the protective overvoltage was defined as 1.4 V, which lies below the upper limit for degradation of the materials’ structures of SOFC cells. The applied overvoltage protects the cell, from above described destroying effects of gasification by CO2, on multiple levels. Elementary oxygen, especially near the electrolyte, removes carbon deposits, but more important in this regeneration method is its purpose of the cell protection. Ni-oxidation potential is significantly decreased due to applied overvoltage, which postpones oxygen and oxygenated species from the catalyst surface. Desorption of gaseous carbon monoxide and carbon dioxide species, which induce further cell degradation, is thus supported and their further adsorption is not inhibited. Next, this voltage brings the cell into electrolysis mode and the input energy forces the reversible Boudouard reaction. This strategy ensured the gasification of carbonaceous species deposited on the catalytic active Ni, without causing the further performance degradation or microstructure modification. To our best knowledge, combination of CO2 and overvoltage is an entirely new method of removing carbon deposits from the anode surface and restoring the cell performance. However, the applying of overvoltage to enhance hydrogen diffusion through metals such as iron and palladium was presented by Andrews and Ubbelohde.50 The overvoltage was maintained constant by continued electrolysis. A review of early studies of ion diffusion through solids can be found in a book by Barrer51. It is worth noting that Petrakopoulou et al.52 suggested triode fuel cell design, with auxiliary circuit between the anode and the auxiliary electrode. The auxiliary circuit running in electrolytic mode induces an overpotential, thus improving the stability and tolerance of the anode to carbon buildup, since great amount of carbon formed is gasified under applied operating conditions. In the context of the experimental parameters in the present study, the volume fraction of CO2 in nitrogen was 25%. No further gaseous components except CO2 and N2 were used. The input voltage was regulated and the temperature was held constant at 800°C. One regeneration cycle was set to 30 s, but one cycle could not completely remove the carbon and regenerate the electrochemical performance. Thus, several regeneration cycles were repeated in order to achieve the initial cell performance, as shown in Fig. 7a. Initial cell performance is depicted with black solid line, whereas the worsened performance obtained after carbon deposition experiment is always shown with dashed black curve. The gray and green curves between these two curves plot single regeneration steps. It is obvious that stepwise improvement after every cycle ensured the

![Figure 6](image)

**Figure 6.** Electrochemical cell performance and methane reforming (for operation under diesel reformate including 9 vol% CH4) before and after carbon deposition experiments as well as after gasification with carbon dioxide. (a) CO volume fraction at the anode outlet. (b) Comparison of polarization curves.

![Figure 7](image)

**Figure 7.** Electrochemical cell performance and degradation voltage measured after every regeneration cycle (1 (---), 2 (----), 3 (-----), 4 (.........)) with CO2 and protective over-voltage. (a) Comparison of polarization curves before and after carbon deposition as well as after single regeneration steps.
Figure 8. Current measured at the beginning of the gasification process under protective overvoltage: after first cycle (---), after fourth cycle (-----).

Effect of current distribution at the beginning of the gasification process and corresponding to the time of the measured CO-peaks, is visible in Fig. 8. Since the overvoltage forces the electrolysis mode, the current direction differs from the current direction in the load and it is thus shown as negative. The current measured at the beginning of the first regeneration cycle is indicated by gray solid line, such as in diagram above. The first peak shown in the diagram represents the inrush or instantaneous input current, which accrues when the voltage is turned on. The real current distribution is actually depicted after that peak and the current change is given by exponential function. The last regeneration cycle resulted in reduced current, which indicates that the catalytic anode surface is increased and less power is thus needed to remove the adsorbed species from the anode surface. This trend is represented with green dashed line. Furthermore, the carbon gasification during the repeated regeneration cycles was proved by measured CO-peaks with the peak value of approximately 12 vol%, which had the same behavior as the curve shown in Fig. 6b. The same procedure was repeated four times for one single cell and was applied on several cells. This approved the reproducibility of the strategy used.

In order to prove that the applied regeneration strategy did not cause any morphological changes of the cell microstructure and thus to confirm the cell-protecting effect of the applied regeneration strategy, postem-mortem analysis was performed on the examined cells. For this purpose SEM-micrographs and EDX-analysis were taken into considerations. In Fig. 9a SEM image represents the anode surface after the performed regeneration process. It is visible that the anode structure is composed of homogeneously distributed Ni and YSZ phases, and no degradation effects such as YSZ-crushing into small particles and their deposition onto the Ni-catalyst are observed. The fuel electrode’s porosity does not seem to be affected. Two marked points were detailed analyzed by EDX-analysis and the results obtained are represented in Figs. 9b and 9c. Smaller grains, marked with 1, represent YSZ particles, while the Ni-catalyst grains are marked with 2. This morphology analysis showed that no significant changes were detected in the cell’s microstructure, since the anode structure remained porous and homogeneous.

Figure 9. SEM- and EDX-analysis of the anode surface after carbon gasification using CO₂ and overvoltage. (a) SEM-micrograph of the Ni-YSZ surface after carbon gasification. (b) EDX-analysis of the point 1. (c) EDX-analysis of the point 2.
Conclusions

Operation of industrial-sized solid oxide fuel cells under carbon-containing diesel reformate was investigated in this study. The use of the industrially relevant dimension of 10 × 10 cm² should be highlighted here. The cells were fueled under realistic operating conditions using diesel reformate as expected for auxiliary power units as well as modified diesel reformates with increased methane volume fraction. The effect of carbon deposition on the Ni-YSZ anode and a novel regeneration method for its removal were presented. The carbon buildup process on the Ni-catalyst or actually anywhere in the cell fuel supply manifold was detected. Methane including the decreasing steam/carbon ratio was identified as having a major impact on the degradation rate. The critical operating time for carbon deposition process and to reduce the total operating time, the methane amount in the gas mixture used was increased. Detailed microscopic investigation showed that carbon was uniformly formed over the Ni-YSZ-sites. Carbon deposits caused not only degradation of the cell performance, but also changed the Ni-YSZ structure. Crushing of YSZ-particles and their deposition on the Ni-catalyst were determined as a degradation phenomenon that occurred.

A very important part of this study is examination of carbon removal using carbon dioxide as a gasification agent. The results obtained show that carbon dioxide has a strong influence on the degradation of the electrochemical and catalytic performance, due to catalytic action in the anode offgas. In order to accelerate the carbon deposition process and to reduce the total operating time, the methane amount in the gas mixture used was increased. Detailed microscopic investigation showed that carbon was uniformly formed over the Ni-YSZ-sites. Carbon deposits caused not only degradation of the cell performance, but also changed the Ni-YSZ structure. Crushing of YSZ-particles and their deposition on the Ni-catalyst were determined as a degradation phenomenon that occurred.

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