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# Anode regeneration following carbon depositions in an industrial-sized anode supported solid oxide fuel cell operating on synthetic diesel reformate

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## HIGHLIGHTS

- Investigation of commercial-sized cells fueled by synthetic diesel reformate.
- Carbon is formed under load and no fast carbon formation process is applied.
- Cell-protecting regeneration method of carbon formations is demonstrated.
- The applied regeneration method enables the usage of SOFCs in various energy systems.

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## ABSTRACT

Carbon deposition is a primary concern during operation of solid oxide fuel cells (SOFCs) fueled with carbon-containing fuels. It leads to cell degradation and thus reduces SOFC sustained operation and durability. This paper reports on an experimental investigation of carbon formation on the nickel/yttria-stabilized zirconia (Ni/YSZ) anode of an anode-supported SOFC and its regeneration. The cell was fueled with a synthetically produced diesel reformate to investigate and simulate the cell behavior under real operating conditions. For this purpose the cell was operated under load to determine the critical operating time. Rapid carbon generation, such as at open circuit voltage (OCV), can be prevented when the cell is under load. Carbon depositions were detected using scanning electron microscopy (SEM) and further analyzed by Raman spectroscopy. Industrial-size cells suitable for commercial applications were studied. This study proves the reversibility of carbon formation and the reproducibility of the regeneration process. It shows that carbon formations can be recognized and effectively, fully and cell-protecting regenerated. It indicates the excellent possibility of using SOFCs in the automotive industry as an auxiliary power unit (APU) or combined power-heat unit, operated with diesel reformate, without danger from cell degradation caused by carbon-containing fuels.



## 1. Introduction

Increasing energy consumption requires new energy solutions which offer high efficiency and clean energy generation. In this sense solid oxide fuel cells appear to be one promising energy conversion unit which enables high electrical efficiency through the direct conversion of chemical energy of gaseous fuels into electrical energy and without lossy conversion steps. Since SOFC systems are not Carnot limited, their efficiency is independent of the power plant scale [1]. Therefore, SOFC-systems could be efficiently used for small-scale as well as for large-scale power generation. The overall efficiency can be significantly improved through the utilization of waste heat. In ecological terms a fuel cell system is a low pollution system which produces neither fine particulate matter nor nonmetal oxides [2]. Emissions of nitrogen oxides ($NO_x$) are negligible, because the oxidation and utilization of

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the used fuel occur at temperatures lower than required for $NO_x$ production [3]. Furthermore, since these cells are extremely sensitive to fuel impurities, such as sulfide, chloride and phosphide, which cause rapid degradation of the cell, the used fuels should contain no impurities [4–7]. Therefore, SOFC-operation does not lead to the emission of sulfur oxides ($SO_x$). Owing to their high efficiency, SOFCs require less fuel to achieve a target power, which means less $CO_2$ is emitted to the atmosphere.

To effectively use SOFC-systems in the automotive industry or as a combined power-heat unit, the aim is to use available and favorable energy sources with high energy density. Since SOFCs are operated at high temperatures and have very good catalytic performances, they are suitable for internal reforming and if gaseous fuel is directly used, they exclude demand for the usage of an external reformer [8]. Through this possibility they have a great fuel flexibility. Generally, the used fuels can react catalytically in SOFCs or can be reformed by means of steam- or dry reforming.

To enable an easy access of SOFCs in form of auxiliary power units to the automotive market, the investigation of SOFCs fueled with diesel reformate is important [9]. Still, the operation with diesel reformate involves a risk of carbon depositions on the anode and thus leads to cell degradation. This cell-damaging effect depends strongly on the used anode type or on the catalyst type. The most used Ni–YSZ anode structure has the greatest tendency to adsorb carbon, since the excellent catalyst performance enables carbon formation reactions, such as the reactions shown in Table 1, thus blocking the catalyst surface and further the porous gas channels [10]. Many studies have investigated the phenomena of carbon depositions and their impact on the cell performance, mainly caused by methane whether as pure gas or in a gas mixture [11–14]. Sameshima et al. [15] reported that carbon formation always occurred in proximity to Ni, if $CH_4/CO_2$ mixture is used as fuel, while Chen et al. [16] varied the methane volume fraction in syngas to investigate the cell behavior. In their study it is obvious that the increased methane volume fraction leads to cell performance deterioration and even to irreversible cell degradation (at a methane volume fraction of about 23 vol%). Furthermore, the impact of methane and carbon-monoxide on carbon formation has been reported by Xiao et al [17]. They claim there is a difference between carbon formed by methane and carbon formed by carbon-monoxide. If carbon is formed in methane, the amount of the deposited carbon increases by rising temperature and also carbon formed by methane pyrolysis cannot destruct the anode structure. On the other hand, if carbon is formed in CO, the amount of deposited carbon decreases with increasing temperature. Next, the way carbon is deposited or actually linked to the nickel particles impacts further cell performance, as shown in Ref. [18]. Linking of nickel and carbon particles together in the cermet anode without blocking the gas channels improves the electrical conductivity of the cell, while the carbon depositions in the gas diffusion channels block gas transport and lead to irreversible cell degradation. Xiao et al. [17] disambiguate that Ni in an anode encourages carbon formation, but although other alternative materials can prevent carbon depositions, they would have a negative effect the cell performance. Instead of Ni Gd- and Sm-stabilized ceria-based materials or conducting oxides are often investigated and used for the anode fabrication [19–22]. Another option is the usage of copper, where hydrocarbon deposits fill the gaps between the metal particles thus improving the anode conductivity and simultaneously reducing the impedance, which McIntosh et al. [23] described in their study. Although these materials have the ability to suppress carbon depositions, Ni offers a considerably better conductivity and electrocatalytic performance [24]. The influence of hydrocarbons on the carbon formation has also frequently been investigated [25–27].

**Table 1**
Carbon formation reactions.

| | | |
|---|---|---|
| Dissociation of hydrocarbon | $C_nH_m \rightarrow nC + \frac{m}{2}H_2$ | (1) |
| Methane dissociation | $CH_4 \rightarrow C + 2H_2$ | (2) |
| Boudouard reaction | $2CO \rightleftharpoons C + CO_2$ | (3) |
| Carbon-monoxide-reduction | $CO + H_2 \rightleftharpoons C + H_2O$ | (4) |

In this paper, the cell operation with carbon containing diesel reformate is demonstrated and the phenomena of carbon deposition was scrutinized under load in contrast to numerous studies [28–31] which investigated it at OCV. They mainly show that carbon is first linked to nickel and blocks the nickel, while in our study carbon formed under load covered both Ni and YSZ uniformly. Subsequently, this study is initiated to investigate complete and cell-protecting regeneration of formed carbon, since many researchers show how the carbon formation could be reduced, but very few studies suggest, how the cell could be regenerated. To reduce carbon formation due to operation with carbon-containing fuels Mermelstein et al. [32] suggest increasing the current-density and the steam content, while Singh et al. [33] show in their simulation that a critical current density exists and if this current density is achieved, carbon cannot be deposited on the cell surface. With regard to this, Alzate-Restrepo et al. [10] showed that the amount of carbon formed under load was around 100 times less than the amount of carbon formed at OCV and this carbon was also more reactive. Further parameter which can prevent carbon formations is a steam/carbon ratio (S/C); S/C greater than 2 should disable carbon formation, but due to fuel dilution the cell performances are significantly decreased [34]. An increasing amount of $CO_2$ in the fuel gas is also possible for minimization of the carbon formation [18]. Beside the described methods for the reduction of carbon formations, there are some studies which suggest possibilities for carbon removal. Tim et al. [26] suggest an operation with high amount of water-vapor, while Alzate-Restrepo et al. [10] and Horita et al. [35] claim that oxygen anions as well as produced water could regenerate the cell due to reaction with the formed carbon, but neither of them describe the cell performance after the possible regeneration. Kirtley et al. [36] did in situ Raman studies of carbon removal using $H_2O$, $O_2$ and $CO_2$ as gas phase reforming agents. $H_2O$ is demonstrated as the most effective at removing carbon, followed by $O_2$ and $CO_2$. Still, after carbon removal Ni was oxidized thus inducing the increase of the anode volume and adding mechanical stress to the anode, which finally leads to cell damage.

It is important to mention the size and the shape of the cells. A lot of studies have investigated different effects on the solid oxide fuel cells, but mainly on cells with a small active area that do not exceed 16 $cm^2$ and which are button-shaped. The studies, which involved experiments with large area planar single SOFCs, showed that it is more difficult to reach optimal operating conditions and excellent cell performance due to many different factors (such as cell sealing, the contacting, etc.), opposed to small area button cells [37–39]. They further show that the operating conditions strongly affect the electrochemical performance of large planar cells. To ensure the usage of planar SOFCs for stationary, mobile and military application, development of low-cost oxidation-resistant metallic alloys for interconnection purposes is still a challenge [40]. In this study large planar industrial-sized 10 × 10 $cm^2$ SOFCs with an active area of 81 $cm^2$ were investigated, which are thus of great importance as a candidate for the commercial usage in APUs. Since