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Analysis of possibilities for carbon removal from porous anode of solid oxide fuel cells after different failure modes

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HIGHLIGHTS

- Feasibility study of carbon removal from the anode after different failure modes.
- Simulation of different failure modes.
- Experimental determination of carbon formation on planar industrial-sized SOFCs.
- Thermodynamic analysis of carbon formation in form of graphite and carbon nano fibers.

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ABSTRACT

This study focuses on the investigation of possibilities for carbon removal from the fuel electrode of anode supported solid oxide fuel cells (ASC-SOFCs) after different degradation modes. To design the conditions which generally lead the cell in the range of carbon depositions the performed thermodynamic calculations show that the SOFC operating temperature range seems to be appropriate for formation of elemental carbon in various types. Concerning this the loaded large planar single SOFCs are fed with synthetic diesel reformate thus simulating realistic operating conditions and enabling the formation and deposition of carbon on the anode side. A mixture of hydrogen/water vapor/nitrogen is used to remove the detected carbon depositions in a cell-protecting manner. For the purpose of this investigation several failure modes are induced after which determination the already defined regeneration strategy is applied. The cathode degradation is first induced and secondly the fuel supply is interrupted to induce re-oxidation of nickel (Ni) on the anode side. The undertaken investigations determine that carbon can be fully removed from the anode surface after nickel oxidation, while cathode degradation disables the complete cell regeneration.

1. Introduction

Solid oxide fuel cells represent a very attractive technology for clean-power generation by conversion of chemical energy of gaseous fuel into electricity. High operating-temperatures and very good catalytic performances of the porous anode enable high fuel flexibility and internal reforming of hydrocarbons as major advantages of these cells. Due to this feature SOFCs may be regarded as fuel cells with the highest fuel flexibility. A high-efficiency and utilization of waste heat for improving of the overall-efficiency make SOFCs suitable candidate for application in both small-scale and large-scale generation systems [1].

Nickel is the commonly used material on the anode side because of its very good catalytic performance and high electrical conductivity [2,3]. Based on the high operating temperatures of SOFCs, nickel is highly appropriate as catalyst for chemical and electrochemical reactions [4]. Nevertheless, the operation of Ni-cermet based ASC-SOFCs with fuels containing carbon includes the risk of carbon formation on the anode-side. Deposited carbon can block the pores on the fuel electrode and thus obstruct the gas transport through the porous anode, or cover the nickel-catalyst and three-phase-boundary and for this reason the chemical and electrochemical reactions as well as current generation can be inhibited [5]. In some cases, carbon formation can cause irreversible

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degradation of the cell performance and damage the cell micro- and macrostructure [6]. Many researchers investigated an impact of different fuels with carbon contents and showed their degrading effect on the cell performance [7–14]. All these studies confirm a destructive influence of carbon-containing fuels, especially of methane as a fuel component. A very important step in investigation and understanding of carbon deposition process provided in situ optical studies – vibrational Raman spectroscopy, Fourier-transform infrared emission spectroscopy (FTIRES) and near-infrared thermal (NIR) imaging, see Refs. [15–19]. The methods described in these studies were used for direct monitoring of the cell to give information about gas-phase and adsorbed species during operation in real time thus determining the structural and chemical changes of the SOFC anodes. In their studies, the authors showed that methane leads to very fast carbon formations in a wide temperature range, while the carbon growth is reduced by usage of a biogas mixture. For better understanding of carbon formation processes a detailed description of SOFC mechanisms, especially internal reforming of methane – both dry and steam reforming and autothermal oxidation – and the water-gas shift reaction for Ni-YSZ based anode can be found in Refs. [20–22]. The authors developed comprehensive numerical approaches which elaborately describe gas–surface interaction mechanisms. The mechanisms of carbon formation is furthermore described with elaborate detail in Refs. [23,24]. Many researchers describe how the carbon formations could be reduced or even totally disabled. The influence of the current density is frequently scrutinized as a crucial factor for the carbon deposition rate, as shown in Refs. [25–28]. Furthermore, not only the enhancement of current density is proposed for the minimization of carbon depositions, but also the increase of the steam content in the gas mixture used. Even though this could reduce the carbon formation, the increase of volume fraction of steam would dilute the fuel and thus decrease the overall efficiency of the fueled cell. Although many studies show how the carbon formation could be minimized or even stopped, the investigation and development of strategies which assure entire cell regeneration without deterioration of the cell performance and microstructure is still a challenge. The aim of the present study is to carry out the carbon removal from the porous SOFC anode after different failure modes thus determining the feasibility of the regeneration strategy used. In this way it should be clarified if non-limited operation and enhancing of the lifetime of SOFCs could be ensured. To reach the cell operation under carbon formation conditions thermodynamic analysis was undertaken. With this in mind, the thermodynamic study was based on the formation and deposition of carbon on the SOFC-anode due to operation with carbon-containing fuels, especially with a synthetic diesel mixture, the composition of which corresponds to the commercially used diesel reformat, and further on applying the cell-protecting carbon removal strategy. For this purpose, several failure modes were induced to analyze the possibility for carbon removal after different failure modes. Timmermann et al. [12] describe in their study the carbon formation on the cell fed with a model reformat from liquid hydrocarbons as well as carbon removal from the anode. The regeneration was performed with a mixture of 30% H_2O, 57% N_2 and 13% H_2 at 650 °C for 30 min and no carbon particles were found on the cell after the experiment. The cell performances after the carbon removal are not shown. Alzate-Restrepo et al. [26,27] suggest oxygen ions for the fast regeneration of the cell. It should also be considered, that some regeneration strategies could lead to the further cell degradation, for example if H_2O, CO_2 or O_2 are used as carbon gasification agents, once the carbon is removed, an excessive presence of O^{2-} from these agents can oxidize Ni-anode thus leading to the anode volume increase and additional mechanical stress to the anode, see Ref. [29].

In our previous study ([30]) we showed a regeneration strategy for the gasification of carbon formed and deposited by feeding with synthetically produced diesel reformat. The applied regeneration method enabled cell-protecting carbon removal without morphological changes on the cell and returned the cell performance to the initial state. In this study, different failure modes – Ni-oxidation and a cathode degradation – were simulated and the feasibility of the already successfully applied carbon gasification strategy was determined.

2. Experimental

2.1. Cell geometry

Commercial anode supported SOFC single cells with the chemical active area of 81 cm^2 were analyzed in this study. The anode substrate was porous Ni-YSZ with a thickness of approximately 200 μm, on which an anode functional layer (Ni/ZrO_2 with a thickness of approximately 10 μm) was applied. The solid oxide electrolyte fabricated as 10 μm thick YSZ layer conducts the oxygen anions from the cathode to the anode, while the 30 μm thick cathode layer produced as lanthanum strontium cobalt ferrite (LSCF) reduces oxygen to oxygen anions. Fig. 1 shows the scanning electron micrograph (SEM) of the cross-section of the cells used.

2.2. Experimental setup

The experimental setup consists of gas control systems equipped with separate mass flow controllers for the anode supply – nitrogen, hydrogen, carbon-monoxide, carbon-dioxide and methane – and a humidifier unit, based on the water bubbler principle, for the humidification of the fuel gas, but by bypassing CO_2, as well as air supply for the cathode side. The fuel and air flow along the cell in co-flow condition. The single cells were mounted in the alumina housing suitable for testing of the $10 \times 10\ cm^{-2}$ cells. Nickel mesh was used as the current collector on the anode side, while the cathode was contacted with a platinum mesh. The ceramic cell housing was embedded in a temperature-programmed furnace. The gas composition before and after the cell was continuously measured with a gas analyzer. An impedance analyzer with a ±40 *A* booster was used for the electrochemical impedance spectroscopy. The measurements were performed under different load values – mainly over the whole effective load range in a

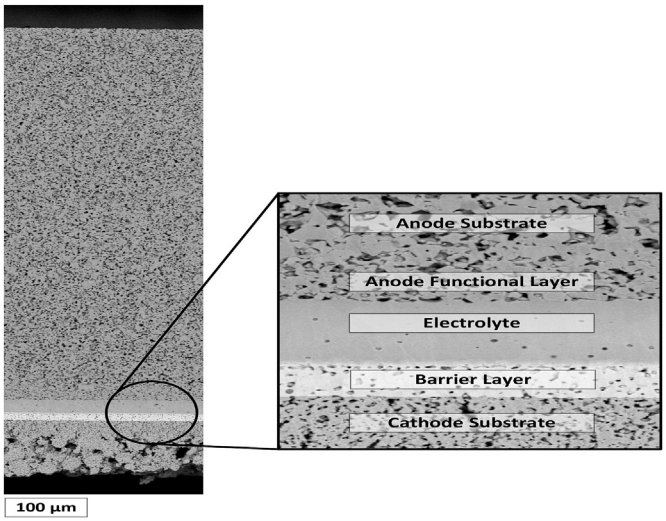

Fig. 1. Scanning electron micrograph of the cross section of the cell used.