



Sulfur poisoning of Ni/Gadolinium-doped ceria anodes: A long-term study outlining stable solid oxide fuel cell operation

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HIGHLIGHTS

- Stable long-term operation of Ni/CGO anodes under sulfur poisoning is possible.
- Degradation is caused by combined sulfur poisoning and large anode overpotentials.
- Ni depletion is observed at critical operating conditions.
- Degradation of the ohmic resistance is observed for sulfur exposure times of 1000 h.

ARTICLE INFO

Keywords:

Solid oxide fuel cell (SOFC)
Ni/CGO anode
Sulfur poisoning
Degradation
Microstructure
Ni depletion

ABSTRACT

This work presents an analysis of the long-term behavior of nickel/gadolinium-doped ceria (CGO) anode-based solid oxide fuel cells (SOFC) under sulfur poisoning conditions. A parameter study of sulfur-induced irreversible long-term degradation of commercial, high-performance single cells was carried out at 900 °C for different H₂/N₂/H₂S fuel gas atmospheres, current densities and Ni/CGO anodes. The poisoning periods of the cells varied from 200 to 1500 h. The possibility of stable long-term Ni/CGO anode operation under sulfur exposure is established and the critical operating regime is outlined. Depending on the operating conditions, two degradation phenomena can be observed. Small degradation of the ohmic resistance was witnessed for sulfur exposure times of approximately 1000 h. Moreover, degradation of the anode charge transfer resistance was observed to be triggered by the combination of a small anodic potential step and high sulfur coverage on Ni. The microstructural evolution of altered Ni/CGO anodes was examined post-mortem by means of SEM and FIB/SEM, and is correlated to the anode performance degradation under critical operating conditions, establishing Ni depletion, porosity increase and a tripe phase boundary density decrease in the anode functional layer. It is shown that short-term sulfur poisoning behavior can be used to assess long-term stability.

1. Introduction

Although their lifetime and performance is continuously improved, solid oxide fuel cells (SOFC) keep on struggling with commercialization. One possibility to decrease SOFC system costs would be to reduce the number of upstream fuel processing components, such as the desulfurization unit. However, sulfur-containing species are present in most of the prospective SOFC fuels such as natural gas and biogas and they lead to significant performance decreases after their exposure to nickel-based anodes.

Sulfur poisoning of the most commonly employed Ni/Yttria-stabilized zirconia (YSZ) cermet anodes has been widely investigated, both

experimentally and theoretically [1–10]. Typically, a rapid, mostly reversible initial drop in power output is observed. This is followed by an irreversible long-term degradation in many cases. The few long-term sulfur poisoning studies existing in literature have focused on the Ni/stabilized zirconia anodes, whose poor long-term stability was demonstrated for the exposure to H₂S over a couple hundreds of hours entailing significant voltage drops caused by a loss of Ni percolation at the anode/electrolyte interface [2,3]. Therefore, there is a considerable interest in the development of more sulfur-tolerant anodes [11–15].

In this regard, Ni/Scandia-stabilized zirconia (ScSZ) anodes were shown to display a higher long-term stability under sulfur exposure than Ni/YSZ, which was related to the higher ionic conductivity of ScSZ

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and the associated lower anode charge transfer resistance [2,16]. However, less studies have targeted the investigation of the sulfur poisoning behavior of Ni/Gadolinium-doped ceria (CGO) anodes although they show a considerably higher short-term sulfur tolerance than Ni/stabilized zirconia and are currently used in several commercial applications [17–22]. Several research groups have experimentally investigated the short-term influence of sulfur-containing fuels on Ni/CGO-based SOFC performance [17–20,23–25]. In these studies the sulfur poisoning behavior of Ni/CGO was found to be promising due to lower performance drops and full reversibility of the poisoning.

Recent studies have indicated fundamental differences in the fuel oxidation mechanism of Ni/CGO and Ni/stabilized zirconia anodes [24,26–28]. At common SOFC operating temperatures and under reducing atmosphere, CGO is a mixed ionic/electronic conductor (MIEC) due to the oxidation state of cerium which can easily hop between Ce^{3+} and Ce^{4+} . Furthermore, CGO shows high surface activity towards hydrogen oxidation. Therefore, the rate-determining charge transfer reaction in Ni/CGO anodes during hydrogen oxidation was suggested to occur at the CGO/gas phase double layer (DPB) rather than at the triple phase boundary (TPB) between Ni/CGO/gas phase. In some of these studies, Ni was even proposed to act merely as electronic conductor [26–30]. However, in our recent work we have shown a considerable poisoning effect on Ni/CGO, thus, concluding that Ni still actively contributes to hydrogen dissociation and/or to the charge transfer reaction as an (electro-)catalyst [24,25]. Moreover, we have shown that, in contrast to Ni/YSZ, Ni/CGO anodes are even able to convert carbon monoxide on the CGO surface under severe sulfur poisoning conditions [25].

Despite the increasing number of fundamental studies of Ni/CGO anodes, the mechanism of hydrogen electro-oxidation remains unknown and the interplay with H_2S not clearly understood. Moreover, most studies focused on the underlying fuel oxidation and poisoning mechanism and there are no reports about the long-term sulfur poisoning behavior of Ni/CGO anodes. The identification of irreversible degradation processes induced by sulfur poisoning can only occur through long-term tests with operation times above several hundred hours. This is vital to characterize the acceptable limits of sulfur impurities in carbon-containing fuels which are relevant for SOFC system operation.

Thus, this work presents the results of long-term degradation experiments of Ni/CGO-based anodes exposed to a variety of H_2S -containing $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ fuel mixtures at 900 °C. The degradation behavior is monitored *operando* by means of electrochemical impedance spectroscopy. Furthermore, a 3D reconstruction technique using focused ion beam (FIB)-scanning electron microscopy (SEM) tomography is applied for quantitative characterization of the microstructural evolution of the Ni/CGO composite anode during the long-term tests, which is then correlated to the anode performance degradation.

2. Experimental methodology

2.1. Solid oxide cells

The tested SOFC are commercial, electrolyte-supported cells with dimensions of $50 \times 50 \text{ mm}^2$ and an active surface area of $40 \times 40 \text{ mm}^2$. The cells stem from different suppliers and consist of slightly different geometries and materials. An overview of the different cells is given in Table 1. Cell A and cell B both employed a Ni/Ce_{0.9}Gd_{0.1}O_{2-δ}(CGO10) anode and an additional 5 μm thick CGO10 adhesion layer between electrolyte and functional anode layer. Furthermore, a current collector layer with increased Ni content was utilized. Both cells were characterized in detail by means of current-voltage characteristics, electrochemical impedance spectroscopy (EIS) and SEM in our previous publications [24,25].

Furthermore, two other cell types based on a Ni/YSZ and a NiCu5/CGO40 anode were investigated. However, their investigation is not the

Table 1
Geometries of the SOFC used in the present study.

Cell name	Manufacturer	Anode	Electrolyte	Cathode
Cell A [24,31]	Kerafol	Ni/CGO10 (25 μm)	3YSZ (90 μm)	LSM/3YSZ (65 μm)
Cell B [25,32]	IKTS	Ni/CGO10 (20 μm)	10Sc1CeSZ (160 μm)	LSMM/ 10Sc1CeSZ (50 μm)

main focus of the present study. Still, the respective experiments are briefly summarized in section 3.2, and a detailed explanation of the materials and the experiments are given in the supporting information.

2.2. Electrochemical characterization

The setup for cell testing enables the characterization of up to four cells simultaneously under variation of current density and H_2S concentration and has been illustrated and described in detail elsewhere [24,25,33]. Long-term experiments were performed with different sulfur exposure times between 200 and 1500 h. All tested cells and the corresponding testing conditions are listed in Table 2. If not stated differently, the cells were operated at 900 °C with $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ fuel mixtures and different H_2S concentrations at a constant total fuel flow rate of 1 L min^{-1} for every cell. The cathode was operated with air at a constant flow rate of 2 L min^{-1} . The comparatively high operating temperature was chosen to enable higher operating current densities and to accelerate possible changes in the anode microstructure. H_2S was taken from a pressurized $\text{H}_2\text{S}/\text{H}_2$ bottle containing 150 ppm H_2S . The cells were heated (3 K/min) to 950 °C for sealing and subsequently reduced at 900 °C. Proper sealing of all cells was ensured by confirming the open circuit voltage (OCV) to be higher than 1.22 V in pure hydrogen.

After initial characterization by means of electrochemical impedance spectra, fuel mixtures and current density were adjusted to the desired operating conditions and it was waited until the cell voltage stabilized. Then, the sulfur poisoning experiments were started. Therefore, the cells were exposed to different H_2S concentrations (always given with respect to the total gas flow rate). In order to monitor the degradation process, impedance measurements were carried out. After the desired poisoning time was reached, the hydrogen sulfide supply was switched off, and the gas flow was substituted with pure H_2 to regenerate the anodes. Then, the cells were regenerated until the cell voltage stabilized again.

Electrochemical impedance spectroscopy (EIS) was performed by means of an electrochemical workstation (Zahner[®] PP-240 with Thales software) in a frequency range from 50 mHz to 100 kHz with 8 points per decade. The amplitude of the current stimulus was chosen to be 500 mA and did not trigger a voltage response of higher than 15 mV. SEM images were acquired using a Zeiss Ultra Plus SEM.

2.3. Post mortem analysis

A dual focused ion beam scanning electron microscopy (FIB-SEM; Helios NanoLab 600i, FEI, USA) was employed for 3D reconstruction carried out at the University of Oldenburg. The image acquisition, segmentation and processing was recently described in detail [34,35]. Cells of type A were reconstructed within the present work. The reconstructed volume of the anode of cell A was $11.2 \times 13.1 \times 10.8 \text{ μm}^3$. The respective volumes were reconstructed right next to the anode/adhesion layer interface. The volumes were ensured to be larger than the representative volume element (RVE) to capture meaningful morphological characteristics of the anodes.

X-ray diffractograms were recorded with an X-ray diffractometer, D8 Discover GADDS with a VANTEC–2000 areal detector.

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