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## **Evaluation of the effect of sulfur poisoning on the performance of Ni/CGO based SOFC anodes**

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### **Abstract**

Even though the commonly used Ni/YSZ-based cermet for Solid Oxide Fuel Cell (SOFC) anodes shows high catalytic activity towards the oxidation of a variety of fuels and good long-term stability, it still faces high sensitivity towards exposure to chemical impurities such as sulfur, siloxane and phosphorus. In this regard, Ni/CGO anodes have been shown to display higher resistance to poisoning by chemical impurities than Ni/YSZ anodes. To allow for a deeper understanding of the processes leading to sulfur poisoning in Ni/CGO-based SOFC anodes, this study presents a detailed analysis of SOFC operating on H<sub>2</sub>/H<sub>2</sub>O gas mixtures with trace amounts of hydrogen sulfide (H<sub>2</sub>S).

The short-term poisoning behavior of electrolyte-supported Ni/CGO40-based cells provided by Hexis and commercial Ni/CGO10-based cells was systematically investigated by means of transient voltage stability experiments and electrochemical impedance measurements for a wide range of operating conditions with varying H<sub>2</sub>S concentrations, temperatures, current densities and gas phase compositions. The poisoning behavior was shown to be completely reversible for short exposure times in all cases. By means of impedance spectroscopy it was observed that the sulfur-affected processes show significant different relaxation times depending on the Gd-doping level of the CGO-based anode indicating possible differences in the underlying hydrogen oxidation mechanisms.

Furthermore, in order to evaluate long-term degradation of the cells, voltage stability tests of 900 h were conducted for different H<sub>2</sub>S concentrations. Long-term stability was demonstrated for the low H<sub>2</sub>S concentrations. Throughout these long-term experiments, the degradation processes were monitored by means of impedance spectroscopy. In addition, post-mortem analyses were carried out in order to identify the nature and location of the occurring microstructural changes.

## Introduction

Potential SOFC fuels such as biogas and natural gas usually carry undesirable sulfur-containing compounds that lead to the poisoning of the conventional Ni/YSZ-based fuel electrodes entailing a rapid SOFC performance decrease. [1–4] In this regard, gadolinium doped ceria (CGO) based electrodes possess a higher tolerance toward sulfur poisoning. Despite their superior resistance to a variety of poisons, to date only few studies have been dedicated to the sulfur poisoning behavior of Ni/CGO anodes. [5–12]

While the performance decrease of SOFC with Ni/YSZ anodes was shown to be due to the Ni surface poisoning with elemental sulfur, recent fundamental studies of Ni/CGO anodes have indicated the electrochemistry rather to occur on CGO than on Ni, thus, suggesting the primary role of the Ni phase to be an electronic conductor. [13–15] Since cerium in the CGO based anodes possesses a mixed oxidation state, meaning that it can easily hop between  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ , it provides CGO its mixed ionic electronic conductivity and high catalytic surface activity towards  $\text{H}_2$  oxidation. [5,10,13,16,17]

Several research groups have experimentally investigated the influence of sulfur-containing fuels on Ni/CGO-based SOFC performance. [5–12] However, there is significant discrepancy between these studies concerning the interpretation of the results, in particular regarding the role of Ni. In addition, no studies are available regarding the effect of the CGO doping level to the sulfur tolerance in the SOFC anodes.

In order to shed more light on the sulfur poisoning process of Ni/CGO anodes, in the present work the impact of hydrogen sulfide on Ni/CGO anodes is systematically investigated by means of impedance spectroscopy and voltage stability measurements with varying parameters such as temperature, current density,  $\text{H}_2\text{S}$  concentration and gadolinium doping level of the Ni/CGO anodes.

## Experiments

Two different kinds of electrolyte-supported SOFC (hereafter named as cell A and cell B) were investigated that were both based on Sc-stabilized electrolytes and LSM/ScSZ cathodes. Cell A was produced and provided by Hexis and employs a  $\text{NiCu}_5/\text{Ce}_{0.6}\text{Gd}_{0.4}\text{O}_{1.8}$ (CGO40) anode. Cell B was a commercial SOFC with a  $\text{Ni}/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO10) anode manufactured by Kerafol.

The active area of both planar cells was  $4 \times 4 \text{ cm}^2$  with a total area of  $5 \times 5 \text{ cm}^2$ . Anode and cathode were contacted with nickel and platinum meshes, respectively, in a ceramic cell housing with gold as the sealant between anode and cathode side.

All gases were supplied via mass flow controllers. The  $\text{H}_2$  was humidified in a water bubbler.  $\text{H}_2\text{S}$  was taken from a pressurized bottle containing 100 ppm  $\text{H}_2\text{S}$  in  $\text{H}_2$ . In order to avoid sulfur adsorption on the piping and its dissolution in the water bubbler, the sulfur was injected into the fuel stream after humidification right before the cell housing.

The cells were operated with a  $\text{H}_2/\text{H}_2\text{O}$  fuel mixture in a ratio of 97:3 and different  $\text{H}_2\text{S}$  concentrations at a constant total fuel flow of  $1 \text{ l}\cdot\text{min}^{-1}$  for each cell. The cathode was operated with varying  $\text{O}_2/\text{N}_2$  mixtures, the poisoning experiments were carried out with air and a constant flow of  $2 \text{ l}\cdot\text{min}^{-1}$ .

The cells were heated ( $3 \text{ K}\cdot\text{min}^{-1}$ ) to  $950^\circ\text{C}$  for sealing and the NiO was subsequently reduced at  $900^\circ\text{C}$ . After initial characterization, sulfur poisoning experiments were conducted at  $800^\circ\text{C}$ ,  $850^\circ\text{C}$ ,  $900^\circ\text{C}$  and  $950^\circ\text{C}$  with a current density of  $0.5 \text{ A}\cdot\text{cm}^{-2}$ . For a systematic investigation of the sulfur poisoning behavior, the  $\text{H}_2\text{S}$  concentration was stepwise increased and set to 1, 2, 5, 10, and 20 ppm at each operating point.

The cells were characterized by electrochemical impedance spectroscopy in a frequency range from 100 mHz to 100 kHz with 8 points/decade. The amplitude of the current stimulus was chosen in order to achieve a voltage response not higher than 15 mV.

## Results

A major objective of the present study is to establish the influence of sulfur poisoning on CGO based anodes and to evaluate the role of CGO doping level on the resistance against poisoning. The general approach is to compare different electrochemical measurements employing two types of anodes (cell A and cell B) as mentioned above. Thus, in the following this manuscript firstly presents the extensive analysis of the sulfur poisoning behavior of Ni/CG40-based SOFC (cell A) and subsequently the comparison of these cells and Ni/CGO10-based SOFC (cell B). First, in order to gain an understanding of the behavior of the Ni/CGO40-based cells and to demonstrate their high performance, the cells were thoroughly characterized by means of I-V curves and impedance measurements. Figure 1 reports polarization characteristics of cell A in the H<sub>2</sub>/H<sub>2</sub>O (97/3) mixture and varying temperatures between 800°C and 950°C. As it can be seen the current density at 0.7 V reaches more than 1.1 A·cm<sup>-2</sup> at a temperature of 950°C and still 0.5 A·cm<sup>-2</sup> at 800°C.

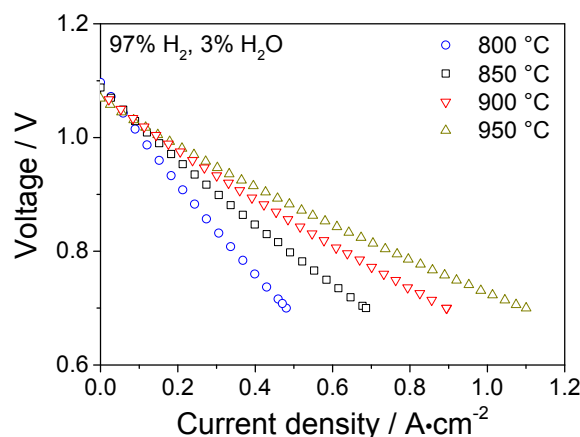


Figure 1: I-V curves at different temperatures  $T = 800^{\circ}\text{C} - 950^{\circ}\text{C}$ ,  $p_{\text{O}_2} = 0.21 \text{ atm}$ , and  $p_{\text{H}_2\text{O}} = 0.03 \text{ atm}$ .

Understanding how hydrogen sulfide partial pressure influences the cell efficiency is an important aspect of establishing the sulfur reaction mechanism. Thus, the electrochemical measurements for sulfur poisoning of cell A anodes are designed to carefully control H<sub>2</sub>S partial pressure with a systematic variation of temperature at 0.5 A·cm<sup>-2</sup>. In order to facilitate the comparison of the poisoning behavior between the different operating conditions, all sulfur poisoning experiments have been conducted with the same cell. As the sulfur poisoning behavior on Ni/CGO anodes is expected to be mainly reversible, this is a viable approach as it is shown in the following. In order to avoid any kind of sulfur-related irreversible degradation, the poisoning intervals were kept as short as possible after saturation of the respective performance drop has been reached. After saturation of the last performance drop related to 20 ppm H<sub>2</sub>S, the sulfur supply was switched off, the respective gas flow substituted with pure H<sub>2</sub> and the anode was recovered until full recovery of the SOFC performance has been achieved.

Fig. 2a+b shows the transient voltage stability tests at 850°C and 900°C. On the right y-axis of the figures the respective imposed H<sub>2</sub>S concentrations are illustrated in blue. The inset in the figure shows only the poisoning stage without the cell recovery with a higher magnification. The oscillation of the cell voltage in the figures is caused by electrochemical impedance measurements that were recorded after the saturation of each performance drop. As it can be seen the voltage drop is stepwise increasing along with the H<sub>2</sub>S concentration. The initial performance drop associated with the exposure of 1 ppm is the largest while the further increase of H<sub>2</sub>S concentration only leads to smaller performance losses. For all investigated operating conditions a reversible degradation is reached which is in contrast to reports on the sulfur poisoning of Ni/YSZ anodes that show the onset of irreversible degradation already for small exposure times. [18]

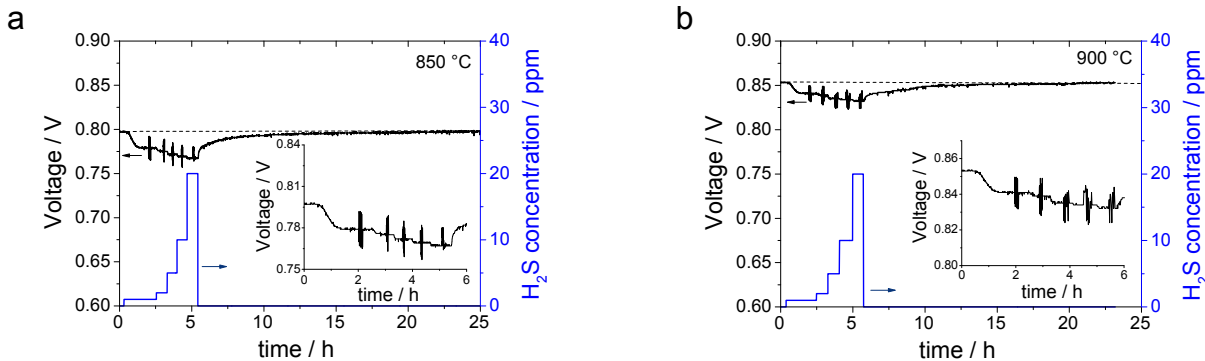


Figure 2: Voltage stability tests during poisoning and recovery phase at  $i = 0.5 \text{ A} \cdot \text{cm}^{-2}$ ,  $p_{\text{O}_2} = 0.21 \text{ atm}$ ,  $p_{\text{H}_2\text{O}} = 0.03 \text{ atm}$ , with stepwise increasing H<sub>2</sub>S concentrations (0–20 ppm), for different temperatures (a) 850 °C, and (b) 900 °C. The inset shows only the poisoning with a higher magnification. The cell voltage is depicted on the left y-axis (black), the H<sub>2</sub>S concentration (blue) on the right y-axis.

In order to compare the degradation behavior in dependence of the operating temperature, the voltage drops and the increase of total cell resistance are depicted for all investigated temperatures over the imposed H<sub>2</sub>S concentrations in Fig. 3. As it can be seen, both Fig. 3a and 3b show the same trend of a lower voltage drop, respectively lower increase of cell resistance with increasing temperature indicating a mitigating effect of temperature on the extent of sulfur poisoning. A similar behavior has also already been observed for sulfur poisoning of Ni/YSZ and can be related to an increasing desorption of H<sub>2</sub>S from the CGO surface with increasing temperature and thus, a reduced sulfur surface coverage. [19] Furthermore, Mullins et al. have indicated the possibility of increasing diffusion of adsorbed sulfur atoms into the bulk phase at higher temperature. [20] The overall voltage drop is smaller than only 40 mV at all operation points demonstrating the high sulfur tolerance of Ni/CGO anodes.

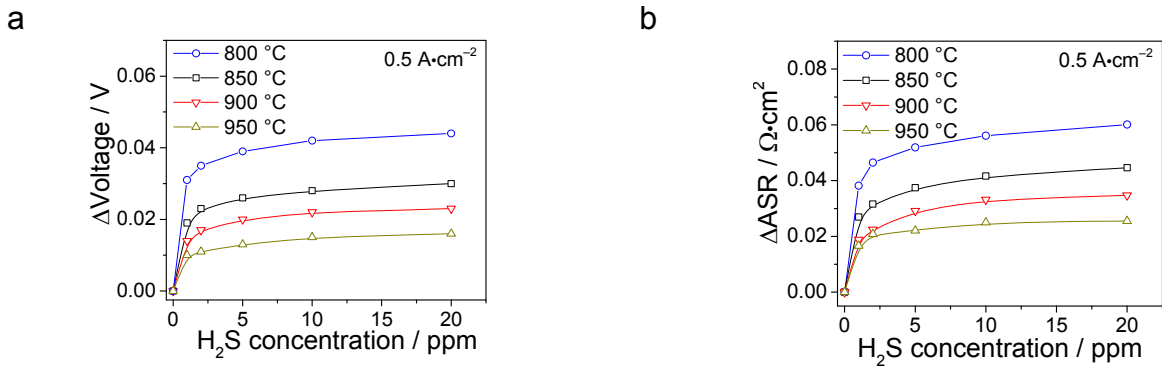
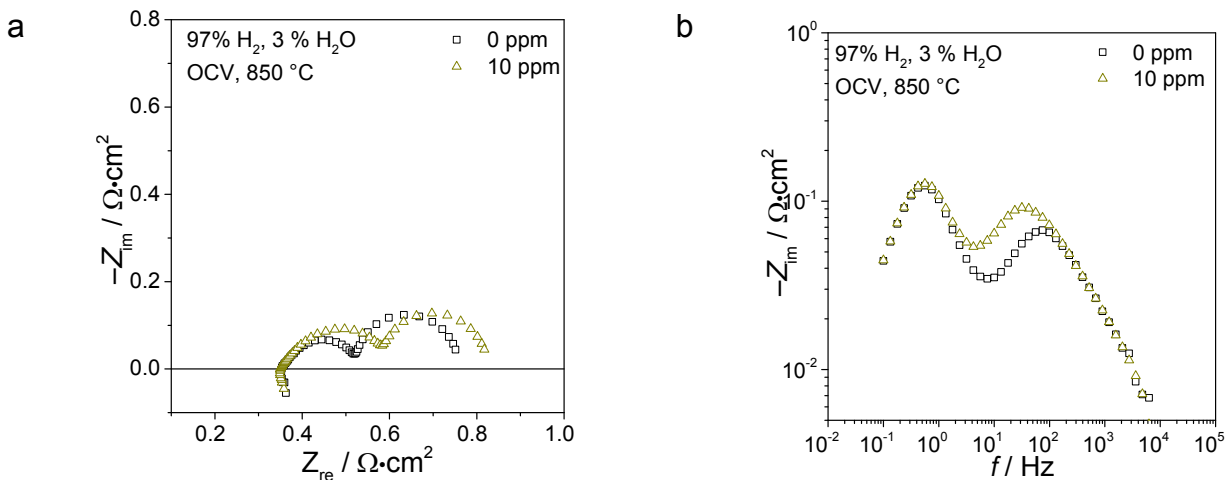


Figure 3: The accumulated (a) voltage drop and (b) total cell resistance increase as a function of H<sub>2</sub>S concentration,  $i = 0.5 \text{ A}\cdot\text{cm}^{-2}$ , and different temperatures  $T = 800 \text{ }^\circ\text{C}$ ,  $850 \text{ }^\circ\text{C}$ ,  $900 \text{ }^\circ\text{C}$  and  $950 \text{ }^\circ\text{C}$ .

In addition, the effect of sulfur on SOFC performance was also investigated for cells with different Gd doping of the CGO in the anode. Therefore, the effect of 10 ppm H<sub>2</sub>S was examined by means of impedance spectroscopy at open circuit voltage. Fig. 5 depicts Nyquist and imaginary impedance plots for 0 and 10 ppm H<sub>2</sub>S concentrations for cell A (Fig. 4a+b) and cell B (Fig. 4 c+d).

While the impedance spectra show that sulfur exposure leads to an increase of the first arc in the Nyquist plot of the Ni/CGO40-based cell, the Nyquist plot for the Ni/CGO10-based cell surprisingly shows an increase of the second arc. Based on the imaginary impedance plot it can be seen that the frequency of the affected anode process changes from approximately 10–100 Hz in the case of Ni/CGO40 to approximately 0.5 Hz in the case of Ni/CGO10. This difference of about two orders of magnitudes indicates that the underlying hydrogen mechanisms in both cases might be fundamentally different. While the peak frequency of the affected anode process at 0.5 Hz for Ni/CGO10 is characteristic for a mixed ionic electronic conductor with a chemical surface capacity, the corresponding peak frequency for Ni/CGO40 is rather uncharacteristic for this kind of process. However, it is also approximately two orders of magnitude smaller than the commonly observed frequency of charge transfer processes at the triple phase boundary (TPB) making a definite assignment of its origin difficult. [21–22]



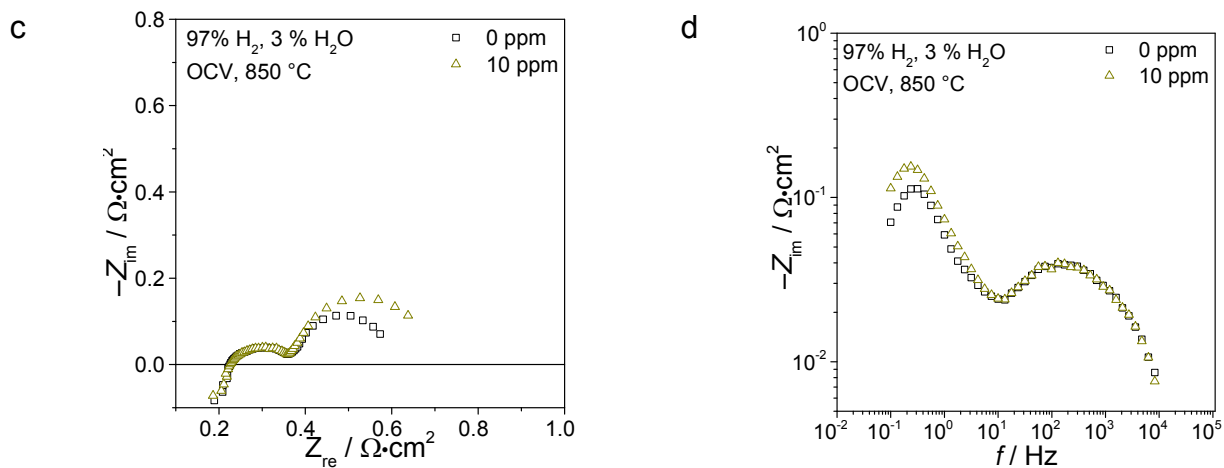


Figure 4. Nyquist and imaginary impedance plot of impedance spectra of a Ni/CGO40-based (a+b) and a Ni/CGO10-based (c+d) SOFC recorded at  $T = 850^{\circ}\text{C}$ , OCV,  $p_{\text{O}_2} = 0.21$  atm,  $p_{\text{H}_2\text{O}} = 0.03$  atm, and varying  $\text{H}_2\text{S}$  concentrations of 0 and 10 ppm.

## Summary and conclusions

In the present work a detailed experimental analysis of Ni/CGO-based SOFC operating on  $\text{H}_2/\text{H}_2\text{O}$  gas mixtures with trace amounts of hydrogen sulfide ( $\text{H}_2\text{S}$ ) was carried out. The short-term poisoning behavior of electrolyte-supported Ni/CGO40-based and Ni/CGO10-based cells was systematically investigated by means of transient voltage stability experiments and electrochemical impedance measurements at different operating conditions varying  $\text{H}_2\text{S}$  concentration, temperature and current density. The poisoning behavior was shown to be completely reversible for short exposure times in all cases. By means of impedance spectroscopy it was observed that the sulfur-affected processes show significant different relaxation times depending on the Gd-doping level of the CGO-based anode.

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