



# Ohmic resistance of nickel infiltrated chromium oxide scales in solid oxide fuel cell metallic interconnects



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## ABSTRACT

Oxide scale formation on metallic interconnects contributes to the overall degradation of solid oxide fuel cell (SOFC) stacks. On the anode side, thermally grown oxide scale might contain additional nickel, nickel oxide, or nickel chromium spinel phases – depending on the applied operation conditions. Ni originates from Ni-meshes, often applied as current collector, from Ni-containing anodes or from Ni-containing coatings. Ni particles released during thermo redox cycles from adjacent Ni-containing components might be interspersed into the oxide scale. This study aims at investigating the influence of Ni on the electrical conductivity of oxide scales. For this purpose pellets of Cr<sub>2</sub>O<sub>3</sub> were mixed with different amounts of Ni and then investigated in-situ under both reducing and oxidizing gas atmospheres at 850 °C. The formed crystals were analyzed using X-ray diffraction, whereas the resulting microstructures were quantified using scanning electron microscopy. During oxidation Ni is converted into NiO, and the latter interacts with Cr<sub>2</sub>O<sub>3</sub> to form a NiCr<sub>2</sub>O<sub>4</sub> spinel phase. Subsequent exposure to reducing conditions leads to an almost instantaneous decomposition of NiCr<sub>2</sub>O<sub>4</sub> spinel, resulting in finely dispersed elementary Ni. This rearrangement of Ni by spinel decomposition leads to a significant improvement of the electrical conductivity of the Cr<sub>2</sub>O<sub>3</sub> pellets compared to their initial state.

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## 1. Introduction

For stationary solid oxide fuel cell (SOFC) applications an average power degradation below 1% per 1000 h operation over a minimal lifetime of 40,000 h is required [1–5]. Recent progress in SOFCs, particularly much improved anode redox stabilities [6,7], has shifted research activities towards the reduction of the ohmic losses caused by oxide scales growing on metallic interconnects (MICs) [8–10].

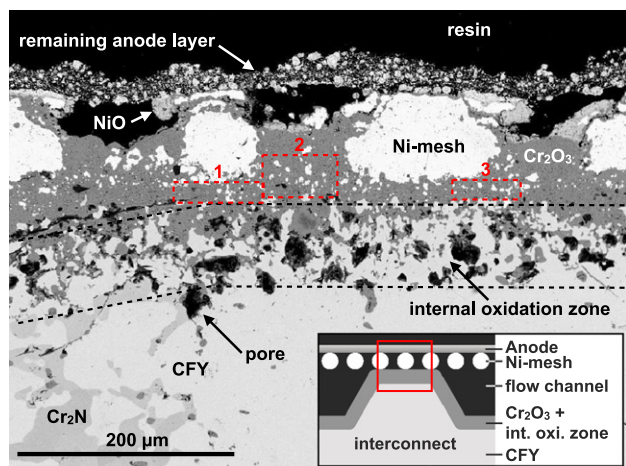
Interconnects separate the fuel on the anode side from the air on the cathode side. They ensure proper gas distribution on the electrodes and collect and redistribute the electrical current from and to the cells, respectively [11–13]. Details about the various requirements imposed on interconnects of SOFC stacks and available materials are described elsewhere [11,14,15].

Significant losses are caused by Cr<sub>2</sub>O<sub>3</sub> scale formation on Cr containing interconnects. This degradation occurs under both oxidizing and

reducing (water containing) conditions [14]. Due to the low conductivity in the range of 0.001–0.2 S cm<sup>-1</sup> [17,18], the oxide layers often provide a major contribution to the overall resistance of SOFC stacks. However, the extrinsic electrical conductivity of thermally grown semi-conductive Cr<sub>2</sub>O<sub>3</sub> is influenced by various parameters including temperature, impurities and variations of the gas composition with the oxygen and water partial pressures as most relevant contributions. (Note: At a temperature below 1000 °C the electrical conductivity of Cr<sub>2</sub>O<sub>3</sub> is dominated by impurities, which is denoted as extrinsic property [18–22]). In our previous publication [15], we presented results for the ohmic losses originating from the cathode side of metallic interconnects. In this work, the focus will be on anodic side MIC degradation. As will be shown, the latter exhibiting greater variation in the microstructures, including possible formation of spinel phases. Additionally the extrinsic electrical conductivities may vary with changing gas composition. If Ni is present on the anode side of a SOFC stack repeat unit the formed Cr<sub>2</sub>O<sub>3</sub> might interact with nickel or nickel oxide. The involved nickel might originate from different sources: the anode [23], the current-collector mesh [14,24–26], or Ni-containing interconnect coatings [25,27–30]. For a chromium based (CFY, [31]) interconnect operated for 40,000 h in a Hexis stack at about 900 °C, Fig. 1 shows a typical

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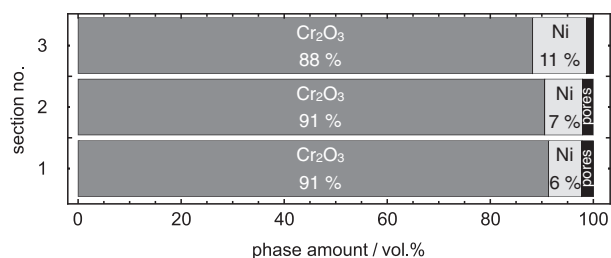
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**Fig. 1.** Cross section of a CFY MIC operated in a Hexis SOFC stack under real conditions at 900 °C for 40,000 h including 15 redox cycles running on CPOx reformed natural gas [14,16].

scanning electron microscopy (SEM) cross section. The image was taken at the top of the interconnect including a Ni-mesh and the remaining anode. The red rectangle in the inset illustrates schematically the SEM image location. Note that the bright spots within the  $\text{Cr}_2\text{O}_3$  matrix are identified as metallic Ni. Obviously, the  $\text{Cr}_2\text{O}_3$  scale formed on the CFY MIC interacts with the Ni-mesh and the Ni containing anode. Note that the observed NiO represented as a light gray color, was formed during shutdown under partly oxidizing conditions. Dashed black lines mark the internal oxidation zone, which together with the  $\text{Cr}_2\text{N}$  formation are typical features of CFY degradation on the anode side [14]. To illustrate the magnitude of the local Ni content in a thermally grown  $\text{Cr}_2\text{O}_3$  layer the phase content for three specific regions was additionally quantified within the red dashed rectangles in Fig. 1. The corresponding phase distributions are shown in Fig. 2. As shown the local Ni content can be rather high, i. e. more than 11 vol.%

It is obvious from Fig. 1 that the ohmic losses associated with oxide scales will depend in a complex way on the microstructure and the distribution of the various phases. In particular, it will depend on the presence of Ni, which has an electrical conductivity several orders of magnitude higher compared with that of  $\text{Cr}_2\text{O}_3$  [17,18,32]. Therefore the motivation of this study is to improve the understanding of the Ni/ $\text{Cr}_2\text{O}_3$  interaction typically occurring on the anode side of MICs with high chromium contents such as for CFY. Electrical conductivity measurements of MIC materials in reduced and/or oxidized gas atmospheres are indispensable to detect their overall degradation behavior. However, the obtained findings are difficult to interpret since they represent a superposition of a number of mechanisms such as oxide scale formation, segregation of reactive elements [33,34], integration of impurities into the  $\text{Cr}_2\text{O}_3$  lattice structure [19,22,35] and spinel formation by alloys. To single out the effect of Ni interaction with  $\text{Cr}_2\text{O}_3$  we used instead pellets, which contained only  $\text{Cr}_2\text{O}_3$ , unavoidable pores and



**Fig. 2.** Phase distribution within thermal grown oxide scale after 40,000 h stack operation for the specific regions marked by red dashed rectangles in Fig. 1.

different amounts of Ni. The later one was systematically varied to take into account the observed wide range of local Ni contents in the anode side oxide scale as observed in Fig. 1.

The electrical conductivities of these Ni containing pellets were studied in situ at different gas atmospheres including redox cycles for an overall period of more than 2000 h, i. e. under long-term conditions. In addition, the thermal activation energy was determined by temperature variations at different points in time. To allow more thorough interpretations, the obtained electrical conductivity denoted as  $\sigma_{\text{eff}}$  and the thermal activation energy  $E_A$  for all experimental data were complemented by microstructure, X-ray diffraction (XRD) and atomic force microscopy (AFM) data as well as information from literature.

## 2. Experimental details

### 2.1. Pellet preparation

To prepare the pellets,  $\text{Cr}_2\text{O}_3$  powder was mixed with different amounts of nickel powder. The resulting compositions and the corresponding labels are summarized in Table 1. Note that the provided values for Ni content correspond to the volume fraction of solids e. g. a pellet with 10 vol.% Ni is denoted as  $\text{Cr}_2\text{O}_3$ -10. For the preparation of the  $\text{Cr}_2\text{O}_3$ -0.5 pellets Nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was mixed with the  $\text{Cr}_2\text{O}_3$  powder. The samples with a Ni content of 5 vol.% and higher were admixed with ball milled metallic Ni particles with an averaged particle size  $r_{50}$  of 5.5  $\mu\text{m}$ . To ease the pellet handling after pressing a few drops of Terpineol were added. The powder was uniaxially pressed with 200 kN at room temperature in a steel die with 40 mm diameter to form 2 mm thick tablets. The tablets were sintered in two batches at the highest available temperatures (for the available equipment) to minimize the porosity. The first batch with the  $\text{Cr}_2\text{O}_3$ -0 pellets was sintered in air for 2 h at 1585 °C. To avoid NiO formation the second batch with the Ni containing pellets was sintered for 2 h in reducing hydrogen atmosphere at 1400 °C, i. e. just below the Ni melting point. The tested  $\text{Cr}_2\text{O}_3$  pellets of size 10–12 mm  $\times$  35 mm after sintering were cut out of the sintered tablets. Note that one  $\text{Cr}_2\text{O}_3$ -5 pellet was broken during preparation hence resulting in two smaller samples of sizes 5–7.5  $\times$   $\approx$  25 mm.

### 2.2. Electrical conductivity measurement

$\sigma_{\text{eff}}$  was measured using a four-point probe set-up in a Gero SR 70-500 tube furnace under various atmospheres overall for more than 2000 h. To adjust the flow rates the set-up was equipped with flow controllers to overflow the samples with the desired atmosphere. The furnace was equipped with a Pt/YSZ/Pt-sensor to record the Nernst potential next to the samples. To monitor the temperature a thermocouple type K was also placed near the samples. Since the used set-up did not provide measuring channels for all samples  $\sigma_{\text{eff}}$  characterization was done in two batches (cf. Table 1).

**Table 1**

Ni content in  $\text{Cr}_2\text{O}_3$  pellets and corresponding labels as used in this work. The test batch column denotes the two different conductivity measurement campaigns (cf. Section 2.2).

Sample #	Ni vol.%	Matrix	Text label	Fig. label	Test batch #
1	0.0	$\text{Cr}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$ -0	0% Ni	2
2					
3	0.5	$\text{Cr}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$ -0.5	0.5% Ni	1
4					
5					
6a	5.0	$\text{Cr}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$ -5	5% Ni	1
6b					
7	10.0	$\text{Cr}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$ -10	10% Ni	1
8					
9	20.0	$\text{Cr}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$ -20	20% Ni	2
10					

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