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# Comparison between $La_{0.6}Sr_{0.4}CoO_{3-d}$ and $LaNi_{0.6}Co_{0.4}O_{3-d}$ infiltrated oxygen electrodes for long-term durable solid oxide fuel cells

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ABSTRACT

The degradation of infiltrated oxygen electrodes during long-term operation of solid oxide fuel cells (SOFCs) was studied. The infiltrated oxygen electrodes were prepared by infiltration of the electro-catalysts $La_{0.6}Sr_{0.4}CoO_{3-d}$ (LSC) and $LaNi_{0.6}Co_{0.4}O_{3-d}$ (LCN) into a porous yttria stabilized zirconia (YSZ) backbone that was pre-infiltrated with a gadolinium doped ceria (CGO) barrier layer. The performance of the infiltrated LSC and LCN electro-catalysts were compared for both symmetrical cells and full SOFCs. Galvanostatic long-term performance tests up to 1400 h at 700 °C and 0.5 A/cm$^2$ were conducted and the change of resistance was followed by electrochemical impedance spectroscopy under current load. The cell performance degradation profiles of the LSC and LCN infiltrated cells showed significant differences. The performance of the LSC infiltrated cell stabilized after 700 h of operation and the LCN infiltrated cell degraded throughout the entire testing period. The difference between the intrinsic properties, i.e. its electrochemical activity, ionic conductivity, and reactivity of LSC and LCN materials was hypothesized to be responsible for the observed difference in the degradation profile.

## 1. Introduction

Solid oxide fuel cells (SOFCs) have the potential to offer high energy efficiency and high fuel flexibility. However, existing SOFC technology requires further maturing to become economically feasible. Consequently, a large effort has been devoted to reducing the operating temperature of SOFCs from 800 °C to 1000 °C to intermediate temperatures of 500–700 °C. With decreasing the operating temperature, the electrochemical resistance of the key components of the SOFC will drastically increase, including the resistance of oxygen reduction reaction. Thus, the development of oxygen electrode materials and structures with high catalytic activity is crucial for bringing SOFC closer to commercialization.

To fulfill this goal, the infiltration of electro-catalyst on the oxygen electrode side was introduced [1,2]. Several different strategies of infiltration to improve the performance of oxygen electrode have recently been comprehensively reviewed [3,4]. One of the most reliable methods is to modify the surface of state-of-the-art oxygen electrodes by introducing nano-sized catalysts via infiltration. However, chemical reactions between some of the infiltrated materials and the oxygen electrode material, despite of high initial improvement, often result in a fast degradation of the electrode performance [5]. Another strategy to prepare an oxygen electrode with high performance by infiltration is using a porous oxide ion conductive layer of the same material as the electrolyte as a backbone structure for the infiltration of an electrically conductive electro-catalyst [2,6–11]. Major advantages of this design are i) the simplification of SOFC processing, as only a single sintering step is needed, ii) a good ionic conductivity between electrolyte and oxygen electrode, iii) a large selection of available electro-catalyst materials and iv) the elimination of the thermal expansion coefficient (TEC) mismatch that is often observed between the oxygen electrode materials and the electrolyte. Besides this, such a design among others represents a platform for the development and study of new electro-catalyst materials with varied infiltration processes and compounds compositions [8,9]. The infiltration process usually requires lower temperature (300 °C–450 °C) for the formation of the required structures, compared to the conventional oxygen electrode preparation methods (e.g. screen printing and hereafter sintering at ~1000 °C). This enables a study of new electro-catalyst materials, which otherwise will react extensively with the electrolyte or decompose thermally at high temperatures [4,6,10].

The reactivity between electro-catalysts and backbone/

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electrolyte material, in this case yttria stabilized zirconia (YSZ), is strongly reduced by using a few-hundred-degree-lower processing temperature. However, strontium and/or lanthanum containing perovskites (like $La_{1-x}Sr_xCoO_3$, $LaCoO_3$ and $LaNiO_3$) will thermodynamically react with $ZrO_2$ forming $SrZrO_3$ and $La_2Zr_2O_7$ within the temperature range relevant for the SOFC operation [12,13]. A direct contact between electro-catalyst and YSZ backbone must therefore be prevented. A successful coating of the YSZ backbone surface with an inert oxide ion conductive material, like gadolinium doped ceria (CGO), has been shown to drastically improve the performance of $La_{1-x}Sr_xCoO_3$ and $LaNi_{1-x}Co_xO_3$ cells [14,15].

The key criterion for the selection of the electro-catalyst for infiltrated electrodes is a high initial performance as well as a low degradation during long-term operation. Based on previous studies [11,16] two electro-catalysts, $LaNi_{0.6}Co_{0.4}O_{3-d}$ (LCN) and $La_{0.6}Sr_{0.4}CoO_{3-d}$ (LSC), were chosen for the long-term SOFC operation studies of the anode supported SOFC with the YSZ backbone infiltrated oxygen electrodes. $LaNi_{1-x}Co_xO_{3-d}$ compounds are good electronic conductors with an electrical conductivity of around 1600 S/cm at 700 °C [17,18], but relatively poor ionic conductors with an ionic conductivity of ca. 0.0006 S/cm at 885 °C [19]. On the other hand, $La_{0.6}Sr_{0.4}CoO_{3-d}$ is a good mixed ionic and electronic conductor (MIEC) with an electronic conductivity of 1900 S/cm [20] and an ionic conductivity of 0.02 S/cm at 700 °C [21,22]. The aim of the here reported work is to directly compare the electrochemical performance and the durability of these two electro-catalysts when infiltrated in a CGO pre-infiltrated YSZ backbone as oxygen electrode and to elaborate on mechanisms and properties that can cause deviation in the cell's degradation profile.

## 2. Experimental

### 2.1. Infiltration of cells

### 2.1.1. Infiltration of symmetrical cells

Symmetrical cells were prepared by co-sintering of three laminated YSZ tapes ($ZrO_2$ with 8 mol. % of $Y_2O_3$): a porous YSZ, a dense YSZ, and a porous YSZ tape. The slurry preparation for the tape-casting and tape fabrication details have been reported previously [23,24]. The tapes for the porous YSZ layer were prepared from a YSZ slurry containing graphite and spherical poly-(methyl methacrylate) (PMMA) particles as pore formers, as described elsewhere [23,25]. After sintering at above 1250 °C the symmetrical cells were laser cut to a size of $6 \times 6$ mm$^2$. The final design and structure of the symmetric cells was 45 μm thick YSZ backbones with porosity of above 60 vol% on each side of a 110 μm thick dense YSZ electrolyte.

The symmetrical cells were sequentially infiltrated with a CGO precursor solution and LSC or LCN precursor solutions, as listed in Table 1. The CGO precursor solution was infiltrated prior to infiltration of the electro-catalyst to form a CGO barrier layer on the YSZ backbone. The CGO precursor solution was prepared from aqueous solutions of cerium and gadolinium nitrate with addition of urea (Merck KGaA, Germany) with a molar ratio of 1:5 = [cation]:[urea] and 2-butanol (5 wt %) to form $Ce_{0.8}Gd_{0.2}O_{1.9}$ after heat treatment. The LSC and LCN precursor solutions were prepared from nitrates aqueous solutions with addition of Pluronic P-123 surfactant (Sigma-Aldrich Corporation, Germany) having 10 wt% of cations to form $La_{0.6}Sr_{0.4}CoO_{3-d}$ and $LaNi_{0.6}Co_{0.4}O_{3-d}$ oxides. The Gd-, Ce-, La-, Ni-, Co-, and Sr-nitrates were supplied by Alfa Aesar, Germany.

The infiltration of symmetrical cells was performed by immersing the cells into the precursor solution for a few seconds. After removing the cells from the solution, the surplus of the solution was wiped off. The solution was removed to prevent clogging of pores in the outer layer of the backbone. First, the symmetrical cells were infiltrated six times with the CGO precursor solution to reach ca. 850 mg of CGO/cm$^3$ in the YSZ backbone. After each CGO infiltration step, the cells were exposed to 350 °C in air for 15 min to dry, decompose nitrates and form CGO nanoparticles. The final heat treatment of the CGO infiltrated YSZ backbone was done at 350 °C for 15 min. The crystal structure and the microstructure of the CGO infiltration layer were published in our previous paper [15]. Hereafter, the cells were infiltrated nine times with the LSC or LCN precursor solutions to reach approx. 690 mg of electro-catalyst/cm$^3$ in the YSZ/CGO backbone. Also, after each electro-catalyst infiltration step, the cells were exposed to 350 °C in air for 15 min.

### 2.1.2. The full SOFC oxygen electrode infiltration

Anode supported SOFC with the YSZ infiltration capable backbone were prepared by co-sintering of four different laminated tapes: a YSZ/NiO support layer, a YSZ/NiO anode, a YSZ electrolyte, a YSZ backbone. A detailed description of the cell preparation has been reported earlier [23,24]. After sintering, the full cells had a 300 μm thick YSZ/NiO support and anode, a 15 μm thick YSZ electrolyte and a 45 μm thick YSZ backbone with a porosity of above 60 vol%. The cells were produced in the size of $13 \times 13$ cm$^2$ which was also used during the infiltration. After the infiltration, the cells were laser cut to pieces of $5.3 \times 5.3$ cm$^2$ to fit into the measurement setup for cell testing.

The YSZ backbone was sequentially infiltrated with a CGO precursor solution and a LSC or LCN precursor solution by using the same precursor solutions as described for the symmetrical cells (section 2.1.1). The infiltration was performed by applying the CGO and LSC or LCN precursor solutions with a brush onto the YSZ backbone side of the full cell. The full cells were *n*-times infiltrated with the CGO precursor solution and *m*-times with the LSC (cell C1) or LCN (cell C2) precursor solutions as listed in Table 2. After each infiltration step, the cells were exposed to 350 °C in air for 15 min.

In addition to this, for one full cell (C3) a direct infiltration of the LCN precursor solution onto the YSZ backbone was performed, without applying the CGO barrier layer. In this case, the infiltration step was repeated nine-times, as listed in Table 2.

Cell C1 ($13 \times 13$ cm$^2$) was laser cut into four pieces ($5.3 \times 5.3$ cm$^2$). One piece was used as-prepared (C1a). On the second piece (C1b) an additional infiltration of the LCN precursor solution was applied, without removing of solution surplus with the intention of generating a thin current collector layer on top of the porous backbone. On the third piece (C1c), after the additional infiltration of the LCN precursor solution (the same as for the C1b), an LCN current collector layer (CCL) was screen printed by using an in-house developed LCN slurry, prepared from $La_{0.99}Co_{0.4}Ni_{0.6}O_{3-d}$ (CerPo Tech AS, Norway).

**Table 1**
List of the symmetrical cells with number of infiltration steps (n, m), loading of the infiltrated material, ohmic resistance ($R_s$), and total polarization resistance ($R_p$) with corresponding activation energies ($E_a$).

| Cell | Sol.1 | n | Sol.2 | m | $m$(CGO)/$V$ [mg/cm$^3$] | $m$(LCN or LSC)/$V$ [mg/cm$^3$] | $R_p$ (@700 °C) [mΩ cm$^2$] | $E_a$[kJ/mol] | $R_s$ (@700 °C) [mΩ cm$^2$] | $E_a$ [kJ/mol] |
|---|---|---|---|---|---|---|---|---|---|---|
| LCN | CGO | 6 | LCN | 9 | 850 | 690 | 37 | 97.5 | 312 | 81 |
| LSC | CGO | 6 | LSC | 9 | 850 | 690 | 31 | 112 | 285 | 87 |