Effect of Microstructure on the Degradation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ Electrodes in Dry and Humid Atmospheres

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Abstract

La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ electrode layers with three different microstructures were manufactured by screen-printing, spin-coating and infiltration into a porous Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ backbone. Electrode performance was monitored at 700°C in 20% O$_2$ over periods of 1,600 to 3,860 h by means of electrochemical impedance spectroscopy under open circuit conditions. Reference measurements were performed in dry atmospheres, where significant electrode activation was observed for cells with spin-coated and infiltrated electrodes. Subsequently, the relative humidity level in the surrounding atmosphere was set to 30% and further raised to 60%, thus simulating SOFC operation with ambient air without pre-drying. While no performance loss could be observed in dry atmospheres, significant degradation occurred in humid atmospheres with pronounced differences between degradation rates of half cells with different electrode microstructures. Post-test analyses by scanning electron microscopy (SEM) and transmission scanning electron microscopy (STEM) were employed to identify the causes for the observed differences in degradation behavior. For screen-printed cells, the surface of the degraded electrodes was covered with small crystallites, probably consisting of SrO formed by Sr-segregation and surface precipitation, where humidity was found to be a crucial factor. For spin-coated and infiltrated electrodes, poisoning by impurities (Si, Cr, S) and particle coarsening were identified as potential causes.

Keywords: Cathode, Degradation, Electrochemical Impedance Spectroscopy, Energy Conversion, Fuel Cells, Long-term Stability, Perovskite Phases, Solid Oxide Fuel Cell

1 Introduction

The long-term stability of cells and stacks is an issue of high relevance for the commercialization of the solid oxide fuel cell (SOFC) technology. While it is practically impossible to completely suppress degradation phenomena, considerable R&D effort has been invested in reducing degradation rates to an acceptable level. To aid in this effort, it is necessary to understand the actual mechanisms which underlie the observed degradation phenomena. Such studies, however, are quite challenging since they require long experimental times, especially when degradation processes are slow and become critical only after several thousand hours. For this reason, there are still many open questions on the topic of long-term stability.

Degradation issues can be tackled on a materials basis by developing novel materials with improved stability against...
specific degradation modes. Degradation rates of SOFC electrodes, however, do not solely depend on the material or material combination but also on the electrode architecture and microstructure. Besides the well-known porous electrodes obtained by the screen-printing technique, alternative architectures, such as thin-film layers or infiltrated electrodes, have been developed more recently.

Several methods for thin-film deposition have been reported in literature [1, 2]. A common method for the deposition of thin oxide films is pulsed laser deposition (PLD). A major advantage of this method is the fact that the cation stoichiometry of the ceramic target is well reproduced in the deposited film [1, 3, 4]. This makes the method useful for the preparation of thin electrolytes in anode supported cells, diffusion barrier layers and thin-film electrodes for SOFCs. Disadvantages of the PLD technology are the complexity of equipment and high costs. Upscaling the process for mass production is a difficult task, but attempts for the application of ultrashort laser pulses in industrial production processes have been made [5, 6] and technical approaches have been developed for depositing films on large area substrates [7]. Due to their well-defined structure, PLD thin-film cathodes are frequently used for fundamental investigations of cathode reaction mechanisms [8–11], but have also been suggested as alternative electrode structures for lowering polarization resistances [12, 13]. Alternative thin-film deposition techniques, which might be more easily adapted for mass production of fuel cells, are based on liquid precursors. In these processes, the salts of cations of the desired oxide (mostly metal nitrates, carbonates or acetates) are dissolved in a liquid solution, together with additives improving homogenization and gelation. The solution is then dried to a polymer film, which is transformed into an oxide layer by annealing. There are various ways to adapt these sol-gel methods to the synthesis of oxide thin-films. The most promising methods are dip-coating and spin-coating, which have been employed for the synthesis of thin oxide films with thickness in the sub-µm range. Detailed studies on electrochemical properties of spin-coated or dip-coated thin-film cathodes have been reported by Peters et al. [14], Januschewsky et al. [15, 16], Hayd et al. [17, 18] and Klotz et al. [19]. In [17] and [18], the microstructure (grain size and porosity) of thin-films was optimized by adjusting the temperature profile of the annealing process and in a follow-up study, the long-term stability of such cathodes under the influence of humidity and CO₂ was investigated [20].

Another electrode fabrication method is wet infiltration, which combines the state-of-the-art screen-printing of porous layers with liquid precursor synthesis. Here, a porous backbone structure is impregnated with a liquid precursor solution and annealed to form fine particles with diameters as low as a few nanometers. This technique is widely applied for the synthesis of catalysts, but has also been investigated for the development of SOFC cathodes [21–23]. The infiltration approach has a high flexibility with respect to material combinations and very promising results of impregnated SOFC cathodes have been reported in the literature. For example, the performance of predominantly electronically conducting (La,Sr)MnO₃₋ₓ cathodes was significantly increased by infiltration with mixed ionic-electronic conductors [24]. Mixed conductors like (La,Sr)CoO₂₋ₓ (LSC) and (La,Sr)(Co,Fe)Oₓ₋₀.₆ (LSCF) have also been used as backbones, whereby the performance and stability could be enhanced by infiltration with a catalytically active compound [25] or even with the backbone material itself [26]. Most of the experiments on infiltrated cathodes reported in literature, however, have been performed using electrolyte scaffolds infiltrated with electronically or mixed-conducting cathode materials [22]. Zhao et al. showed that infiltration might mitigate issues originating from the thermal mismatch between cathode and electrolyte materials by demonstrating a high durability of cathodes of La₀.₆Sr₀.₄CoO₃₋ₓ infiltrated into Sm-doped ceria upon thermal cycling [27]. Shah et al. demonstrated a high performance of cathodes with LSCF infiltrated into a Gd-doped ceria (CGO) backbone and investigated optimization strategies [28]. In a follow-up work, Shah et al. investigated the long-term performance of such cathodes at different ageing temperatures in ambient air [29]. In their work, grain coarsening of the nano-particles was identified as the main source of degradation, but a reasonable long-term performance over a period of 40,000 h was predicted. Similar results on the long-term degradation of cathodes of LSCF and LSC infiltrated in scandia-stabilized zirconia were reported by Zhan et al. [30]. Samson et al. performed tests on anode-supported cells with infiltrated cathodes of LSC in CGO and found very stable cell performance over a period of 1,500 h [31].

La₀.₆Sr₀.₄CoO₃₋ₓ (LSC64) is a mixed ionic-electronic conducting ceramic, which has been thoroughly investigated for application as intermediate temperature solid oxide fuel cell (IT-SOFC) cathode. It features high electronic and oxygen ionic conductivity as well as high electro-catalytic activity for the oxygen reduction reaction. Drawbacks are its high thermal and chemical expansion coefficient due to the large cobalt content, reactivity with zirconia-based electrolytes and occurrence of Sr-related degradation phenomena such as surface segregation or volatilization of strontium.

In this work, the performance and long-term stability of LSC64 electrodes with different microstructures have been investigated on the basis of symmetrical button cells. These were fabricated as model systems, which contain LSC64 electrodes with three different electrode architectures: (i) conventional porous electrodes obtained by screen-printing, (ii) thin-film layers prepared by spin-coating and (iii) infiltrated electrodes consisting of a porous electrolyte backbone impregnated with nanoscaled LSC64. The electrodes were characterized by electrochemical impedance spectroscopy with respect to the long-term behavior of their performance in dry and humid atmospheres. In order to identify the causes underlying the observed degradation phenomena, post-test analyses with scanning electron microscopy and scanning transmission electron microscopy were performed on fresh and degraded samples.
2 Experimental

2.1 Sample Preparation

\( \text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95} \) (CGO) was used as electrolyte material to avoid the detrimental formation of Sr/La-zirconates at the electrode-electrolyte interface, which is observed for zirconia-based electrolyte materials [32,33]. Electrolyte substrates of CGO were prepared from commercially available powder (Treibacher Industrie AG, Austria). The powder was uniaxially pressed in a 2 cm steel die, followed by isostatic pressing at 300 MPa. The disks were sintered for 10 h at 1,450°C and polished with SiC paper up to a roughness of 600 Grit. Substrates used for sol-gel spin-coating were additionally polished with diamond suspensions (9, 3, and 1 μm particle size) to obtain a mirror-smooth surface. The substrates had a diameter of 1.6 cm and a thickness of 1.6–1.8 mm with relative densities above 96%.

LSC64 powder was synthesized by the spray pyrolysis method at EMPA (Dübendorf, Switzerland) with a \( d_{50} \) of 0.9 μm as determined by laser diffractometry. Screen-printing inks of LSC64 were prepared by mixing the ceramic powder with a terpineol-based ink vehicle (fuelcellmaterials, USA) and subsequent homogenization with a three roll mill. The mass fraction of LSC64 in the resulting ink was 70%. Symmetrical cells with circular electrodes of 1 cm diameter were obtained by screen-printing the ink on both sides of CGO electrolyte substrates with an intermediate drying step at 100°C and sintered for 3 h at 1,350°C. This was mandatory to achieve a good electrical contact for electrochemical characterization, since the lateral electrical conductivity of the infiltrated electrode without current collector would be too low.

For infiltration, a few drops of the precursor solution were placed on the backbone and left for a minute to soak in. Afterwards, surplus precursor liquid was removed and the samples were dried at 100°C and annealed at 500°C for 0.5–1 h. Differential weighing was used to determine the weight gain for every infiltration step, which was repeated 8–10 times until the mass fraction of infiltrated material in the backbone structure reached 8–10%.

Finally, current collector layers of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3–\delta} \) (LSCF6428) were screen-printed on top of the infiltrated layers and annealed for 2 h at 700°C. This was mandatory to achieve a good electrical contact for electrochemical characterization, since the lateral electrical conductivity of the infiltrated electrode without current collector would be too low.

For each of the three electrode architectures, secondary samples were prepared with the corresponding electrode layers applied to only one side of the electrolyte substrates. These were mounted close to the symmetrical cells and were removed at different stages of the long-term study for post-test analyses.

2.2 Electrochemical Characterization

For electrochemical measurements, the symmetrical cells were contacted by gold grids pressed onto the electrodes by spring-loaded flat alumina disks. No reference electrodes were applied in order to avoid the introduction of impedance artifacts (see, e.g., [36, 37]). Short-term characterization was conducted between 500°C and 700°C in dry 20% O₂/Ar in a single-chamber quartz glass reactor by means of electrochemical impedance spectroscopy (EIS) at open circuit conditions, using a Novocontrol Alpha-A frequency response analyzer with Z4 interface for data acquisition. Data evaluation and plotting was performed with Python scripts, using complex nonlinear least-squares (CNLS) algorithms for fitting equivalent circuits to impedance spectra of the symmetrical cells. Equivalent circuit models were set up such that each element (R || Q, Gerischer) comprises both electrodes. Area-specific resistances

Nicholas et al. [35]. For fabrication of the backbone layers, a screen-printing ink of CGO was prepared by mixing CGO powder with a viscous ink vehicle (fuelcellmaterials, USA) with a particle load of 60 wt.%. The ink was screen-printed to form circular electrodes (1 cm diameter) on CGO electrolyte substrates, dried at 100°C and sintered for 3 h at 1,350°C. For infiltration, aqueous stock solutions of nitrate salts of La, Sr and Co (1M) were prepared by dissolving \( \text{La(NO}_3\text{)}_{2}\cdot\text{6H}_2\text{O}, \text{Sr(NO}_3\text{)}_{2}, \) and Co(NO_3)_2 \( \cdot \) 6H_2O in deionized water. The actual concentrations of the stock solutions were determined by complexometric titration with EDTA. After mixing the stock solutions in the appropriate stoichiometric amounts, citric acid (Fluka) was added so that the molar ratio between metal nitrates and citric acid was 0.75:1. Ammonium hydroxide was used to adjust the pH to 5. Finally, a few drops of Erkantol NR were added to improve the wetting behavior of the precursor solution.

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and capacitances of single electrodes were then calculated from the fitting parameters, which can thus be considered as taking the average over two electrodes.

Long-term investigations were performed at 700 °C in 20% \( \text{O}_2/\text{Ar} \) at different levels of humidity (see Table 1) over several thousand hours by EIS in order to investigate the development of the electrode polarization resistance over time and compare the susceptibility of different electrode architectures and microstructures to degradation. For every period the symmetrical cells – together with secondary samples of identical make-up – were investigated between 500 and 1,500 h, depending on the observed degradation rates. At the end of each period, the setup was cooled to room temperature, one of the secondary samples was removed and the experiment continued with the next period. This procedure was used to obtain representative information of the state of the actual sample electrodes at different stages during the long-term experiments.

### 2.3 Microstructural Characterization

Pre- and post-test analyses by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) were used to gain deeper insights into the degradation mechanisms on the micro- to nanoscale. SEM images were recorded with a FEI Versa 3D Dual Beam field emission (FE) microscope with an EDAX energy-dispersive X-ray (EDX) detector and a Zeiss Ultra 55 FE microscope with an EDAX Phoenix EDX detector. SEM pictures were recorded in secondary electron (SE) mode for topographical contrast as well as in backscatter electron (BSE) mode for material contrast. STEM images were acquired with a FEI Tecnai F20 operated at 200 kV using a high angle annular dark field (HAADF) detector for imaging and an EDAX Si(Li) detector for EDX analysis.

Further details regarding the preparation, instrumentation and measurement procedures are given by Perz [38].

### 3 Results and Discussion

#### 3.1 Microstructural Characterization

Figures 1–3 show top view and cross section images of the electrode architectures investigated in this work. The screen-printed electrode (Figure 1) has a thickness of approximately 25 \( \mu \text{m} \) with some voids, which may originate from agglomerates in the starting powder.

![Fig. 1 FE-SEM images in SE mode of a screen-printed LSC64 electrode after sintering for 2 h at 1,050 °C in top view (top) and cross section (bottom).](image)

Pictures of the spin-coated electrode show a corrugated surface structure (Figure 2, top) which forms during drying and gel formation. A characteristic double-layered morphology of the thin film is observed in cross section (Figure 2, bottom). This layered structure is a result of the preparation procedure, which was carried out in two cycles of spin-coating, drying and annealing. The total thickness of the film is around 150 nm. Porous zones between the CGO substrate and the bottom layer and between the bottom and top layer are evident, showing that after annealing at 700 °C a complete densification of the film has not been achieved.

Figure 3 (top) shows a top view image of the infiltrated CGO backbone after impregnation with LSC64, but before deposition of the LSCF6428 current collector. From a cross section image of the infiltrated electrode after application of the current collector, a thickness of 20–25 \( \mu \text{m} \) can be estimated for each layer (Figure 3, bottom).

Platinum layers visible in many of the micrographs were applied as protective coatings during sample preparation for pre- and post-test SEM/STEM analyses.

#### 3.2 Short-term EIS Characterization

Results of short-term characterization of a cell with screen-printed electrodes by EIS between 500 °C and 700 °C are presented in Figure 4. Inspection of the impedance spectra in Nyquist representation suggest the presence of at least three processes, labeled as “hi”, “mid” and “low” arcs according to

| Relative humidity of test gas @ 25 °C | \( p_{\text{H}_2 \text{O}} \) / kPa | Thermostat temperature |
|--------------------------------------|-----------------|-----------------------|
| 1st period – dry atmosphere          | 0               | –                     |
| 2nd period – 30%                    | 0.935           | 6 °C                  |
| 3rd period – 60%                    | 1.938           | 17 °C                 |
their peak frequencies lying in the high-, middle- and low-frequency region of the spectrum. Equivalent circuits used for CNLS-fitting are shown as insets. Real-axis offsets (ohmic resistance $R_0$) are due to the electrical resistance of the electrolyte and the electrodes as well as the gold contacts, while the inductivity ($L_0$) is mainly caused by the wirings of the setup.

According to the common interpretation proposed in literature for mixed ionic-electronic conducting electrodes (see, e.g., [39]) the high-frequency arc is ascribed to the charge-transfer process of oxygen ions between the electrode and the electrolyte, while the mid-frequency region is attributed to the actual electrode reactions, which consist of a series of elementary steps such as adsorption of molecular oxygen, dissociative reduction and incorporation of oxygen ions into the crystal lattice [40]. At temperatures of 500°C and 600°C the electrode contribution can be well fitted by a Gerischer element (G) [41], while at higher temperatures the correct impedance representation – if judged on the basis of least-squares fitting quality – becomes more ambiguous and the mid-frequency arc can be equally well represented by a $R\parallel|Q$ element (parallel combination of a resistance $R$ with a constant phase element (CPE) $Q$). A small systematic deviation between impedance data and the model curve is visible at 500°C, which might be caused by slight deviations from perfect cell symmetry implicitly assumed in the impedance models.

The low-frequency arc corresponds to an almost perfect semicircle and may be ascribed to a bulk process involving the gas phase, based on its large capacitance value of approx. $2\,\text{Fcm}^{-2}$ per electrode and the distinctively low activation energy [42–44]. This weak temperature dependence is in contrast to the thermally activated high- and mid-frequency processes (see Figure 5), which renders the low-frequency arc increasingly prominent at higher temperatures. It should be noted that a low-frequency semicircle is also observed in the impedance spectra of cells with spin-coated and infiltrated electrodes with almost identical resistive and capacitive parameters and a similarly weak temperature dependence (see Figures 7 and 9), which suggests that it originates from the measurement setup and not from the sample. It is most likely caused by concentration polarization due to gas exchange limitations between the reactor volume and the electrode surface as a result of pressing flat gold grids onto the electrodes by means of unstructured alumina disks without any gas channel profiles [45]. In this case, there would be insufficient gas exchange between the gas trapped in the meshes of the gold grid and the surrounding atmosphere, leading to a local change in the oxygen partial pressure at the electrodes upon passage of a low-frequency current. Following this assumption and adapting the theoretical treatment presented by Primdahl et al. [44] to the situation at hand yields Eq. (1) for the area-specific capacitance.
where \( F \) is the Faraday constant, \( R \) the ideal gas constant, \( T \) the absolute temperature and \( p_{O_2} \) the oxygen partial pressure in the reactor (0.2 bar). \( L \) is the thickness of the gas layer trapped between the electrode surface and the alumina disk, which is essentially the thickness of the gold grid (0.2 mm).

Plugging these values into Eq. (1) for temperatures between 500 °C and 700 °C yields capacitances of \(~1 \text{ F cm}^{-2}\), in good agreement with the values obtained by EIS. Of course, the gold grids used as current collector do not behave as completely gas-tight seals, and the resistive component of the low-frequency arcs stems from the oxygen exchange between the trapped gas layer and the reactor volume. Since the magnitude of this leakage flow is unknown, the value for the concentration polarization resistance is difficult to estimate.

Figure 5 shows the temperature dependence of the area-specific resistances (ASRs) and capacitances of the three polarization contributions, where capacitance values have been calculated from the impedance expressions of the Gerischer and \( R | Q \) elements according to equations given by Adler et al. [41] and Fleig et al. [46], respectively.

Impedance spectra of the symmetrical cell with spin-coated electrodes at different temperatures are depicted in Figure 6. At 500 °C and 550 °C, the spectra could be well fitted by a series of two \( R | Q \) elements. A Gerischer element is not appropriate in representing the mid-frequency arc of thin films, as might be expected based on the ALS model developed for porous SOFC electrodes [41], which interprets the Gerischer impedance (originally derived for solid-liquid electrochemical systems on the basis of a homogeneous reaction-diffusion scheme [47]) as the combination of a gas-electrode surface exchange...
reaction in the pore network with solid state diffusion of oxygen within the electrode matrix. The ALS model yields a Gerischer-type impedance in the limit of an infinitely thick electrode (in practical terms an electrode whose thickness is significantly larger than the electrochemically active zone), which is a condition unlikely to be met in a thin film.

At higher temperatures, an additional arc emerges at the low-frequency side of the impedance spectrum, caused by concentration polarization, due to insufficient flushing of the electrode surface, as described above.

Area-specific resistances and capacitances of the three impedance contributions are plotted as a function of temperature in Figure 7. It is interesting to note that the activation energies of the ASRs of the spin-coated electrode are very similar to those of the screen-printed electrode (Figure 5), while the capacitances of the mid- and high-frequency processes are significantly lower for the spin-coated film.

Nyquist-diagrams of impedance data from LSC64 infiltrated electrodes are shown in Figure 8 for different temperatures. Below 600 °C, the spectra are adequately represented by three $RQ$ contributions while at 600 °C and above the mid-frequency arc becomes too small for reliable fitting and was therefore removed from the equivalent circuit. Systematic residuals in the data modeling may be attributed to small deviations from perfect cell symmetry.

The temperature dependence of the resistive and capacitive parameters obtained by CNLS fitting of the equivalent circuit models to the impedance spectra are depicted in Figure 9. Magnitude and activation energies of the resistive and capacitive components of the high-frequency arc are similar to those found for the spin-coated electrodes. In contrast, the process in the mid-frequency range has completely different characteristics with an activation energy of the resistance almost twice of that observed for the screen-printed and spin-coated
3.3 Long-term EIS Characterization

EIS analysis was used to follow the temporal development of the resistive and reactive components of specific processes in the impedance spectra at 700°C for different humidity levels. In all cases, more or less pronounced activation processes, affecting both the ohmic resistance and the polarization resistance, are visible in the first few hundred hours with very little degradation – if any – observed in the remaining period of the first stage in dry atmospheres (Figure 10). The strong decrease in polarization resistance ($R_{pol}$) during the first few hundred hours for both the spin-coated electrode (Figure 10, middle right) and the infiltrated electrode (Figure 10, bottom right) is due to the low maximum annealing temperatures of 700°C (2 h) used for cell preparation. Since EIS characterization was performed at the same temperature, sintering processes at the electrodes may well have continued throughout the long-term study. The breakdown of the total electrode polarization into single contributions (Figure 10, left column) shows that the electrode activation originates from a decrease in the resistance of the high-frequency process – ascribed to the oxygen transfer between electrode and electrolyte – which indicates a continuous improvement of the electrical contact at the electrode-electrolyte interface, especially during the initial stages of the long-term study. In contrast, very little activation is observed for the cell with screen-printed electrodes, as the final sintering step was carried out at a much higher temperature of 1,050°C.

Interestingly, also the ohmic resistance ($R_0$) is found to decrease drastically in the course of the long-term study for cells with spin-coated and infiltrated electrodes (Figure 10, right column). This obviously cannot be ascribed to re-sintering of the CGO electrolyte substrate and backbone, as they were sintered at high temperatures of 1,450°C and 1,350°C, respectively. However, $R_0$ clearly contains contributions from the electrode layers as well, as evidenced by the strong discrepancy of $R_0$ values between the investigated cells. Moreover, the contribution of the electrolyte substrates to $R_0$ in Figure 10...
should be around 2.5–3 $\Omega \text{ cm}^2$ (depending on the actual electrolyte thickness), based on a total conductivity of 0.032 $\text{S cm}^{-1}$ for CGO with 10 mol. % Gd at 700°C in air [48]. While $R_0$ values of the screen-printed and infiltrated cells are largely consistent with the ionic conductivity of the CGO electrolyte (for the infiltrated cell, $R_0$ also includes the CGO backbone and the LSCF current collector), the ohmic resistance of the spin-coated electrode is almost one order of magnitude higher which may be due to the low lateral conductance of the thin film and its poor contact between the double layers or with the electrolyte substrate (see Figure 2). For the spin-coated cell, sintering or densification processes of the electrode double layers are assumed to be the main reason for the decrease in ohmic resistance. In case of the infiltrated electrodes, it is more likely that sintering processes at the LSCF current collector – within the LSCF layer or at its interface to the infiltrated backbone – are mostly responsible for the pronounced drop in $R_0$. Again, for the screen-printed electrodes, little variation in $R_0$ is found in the first stage of the long-term study due to the high sintering temperature applied during preparation.

Adjusting the gas humidity to levels commonly encountered in undried ambient air (30% and 60% of full $\text{H}_2\text{O}$-saturation at 25°C), initiated a steady increase in the polarization resistance over several thousand hours. Further raising the humidity level from 30% to 60% was found to have little impact on the degradation rates. The actual polarization resistance of the electrodes was calculated as the sum of the mid- and high-frequency components ($R_{\text{pol}} = R_{\text{mid}} + R_{\text{hi}}$), whereas the resistance of the low-frequency arc ($R_{\text{low}}$) was not included since it is caused by the test rig. Throughout the entire study, capacitances of the single processes were not significantly affected by progressive cell degradation.

In some cases, there was difficulty in obtaining a clear-cut separation of circuit elements, most evident in the scattering of $R_{\text{mid}}$ and $R_{\text{hi}}$ values for the spin-coated electrode (Figure 10, middle left). However, considering that their sum ($R_{\text{pol}}$) gives a continuous line is a clear indication of numerical artifacts due to poor parameter resolution by CNLS fitting. Likewise, for the symmetrical cell with screen-printed electrodes (Figure 10, top row) each stepwise decrease in $R_0$ is compensated by a corresponding increase in the high-frequency contribution to $R_{\text{pol}}$ (ascribed to the charge transfer resistance). This is again a result of the inability of the CNLS fitting algorithm to separate both contributions, as their sum shows much less variation over time.

Keeping these fitting artifacts in mind, one can attempt to establish a general picture of the observed degradation phenomena based on data presented in Figure 10. This is straightforward for the screen-printed electrodes, where it is clearly the resistance of the mid-frequency process that starts to increase in humid atmospheres. Soon after switching to 30% relative humidity, the Gerischer element used to model the mid-frequency process in dry atmospheres (see Figure 4), was replaced by an $R\mid \text{CPE}$ component, which was more suitable to describe the impedance data under humid conditions. For the cell with infiltrated electrodes, the mid-frequency process could not be discerned in the impedance spectra in dry atmospheres and only became visible after switching to 30% relative humidity, where it was then steadily increasing. For the spin-coated cell, the picture is less clear, due to the strong...
overlap of arcs in the mid-to-high frequency region. From the impedance analysis, it appears that both the mid- and high-frequency processes are affected by degradation, however, it is unclear whether this is a real effect or caused by the lack in fitting parameter resolution.

Thus, the general picture emerging from impedance analysis is that cell degradation is mainly affecting the mid-frequency electrode processes. This is quite reasonable, considering that for mixed-conducting electrodes this frequency region is commonly assigned to the actual electrode processes encompassing a series of surface-based elementary reactions (molecular oxygen adsorption, reduction, dissociation, and incorporation into the bulk [49]). These reactions are strongly affected by modifications of the electrode surface induced either directly by H2O(g) [50–52] or indirectly by poisoning with critical impurities (Cr, Si, etc.), due to their enhanced gas phase transport in humid atmospheres [53–56].

Leaving aside the stepwise changes in $R_0$ of the screen-printed cell resulting from fitting instabilities, ohmic resistances are not markedly influenced by degradation processes in humid atmospheres, which is as expected.

### 3.4 Post-test Analysis

Post-test SEM analyses of the screen-printed electrodes showed no conspicuous changes with regard to microstructure or composition. However, at higher magnifications a distinctive patterning of the electrode surface is visible on particles in the degraded electrode layer (Figure 11) with interesting morphological features of nanoscale secondary phases growing on the grain surfaces in form of little bumps (top) or in characteristic geometrically shaped patterns (bottom). The latter seems to be the case for individual flat grain surfaces, which could correspond to defined crystal faces where the patterning might follow dedicated crystallographic directions of the underlying grain.

Similar observations have been made for the related perovskite compound LSCF6428 by Oh et al. [51], who investigated the surface of dense polished samples after heat treatment for 50–100 h at temperatures between 600°C and 900°C and reported the formation of submicron-sized particles with different morphologies (rods, triangles and irregular polygons). They also observed directionally aligned particles on unpolished surfaces and suggested that the alignment patterns were corresponding to the surface orientation of the underlying grains. Although they did not explicitly investigate the effect of humidity, annealing was performed in stagnant air, which is expected to contain some level of atmospheric moisture. Interestingly, they observed much less particle formation when annealing in 1% O2/Ar and pure N2 and explained this by the lower oxygen partial pressure but did not consider differences in humidity (or CO2) between ambient air and bottled gases.

Niania et al. [52] heated dense samples of LSCF6428 up to 1,000°C in dry and humid atmospheres and recorded in situ the surface growth of Sr-based segregation phases by high-temperature environmental SEM (HT-ESEM). The particle growth rate was found to be strongly accelerated at higher water partial pressure. They also observed a relationship between crystallite shape, alignment pattern and grain orientation, but due to problems in determining the precise grain orientation, a definitive correlation could not be established.

A statistical evaluation of the correlation between grain orientation and particle formation (with respect to number density and area coverage) was given by Pişkin et al. [57] for LSC64 annealed for 2–5 h at 800°C in stagnant and synthetic air as well as in pure oxygen. For the sample annealed in stagnant air, the authors found similar number densities of particles on grains with orientations close to (001), (101) and (111) but a 3-fold higher area coverage on (001) oriented faces (assuming ideal Pm-3n crystal structure and allowing for 10° angle tolerance in surface orientation). Unfortunately, the effect of humidity was not included in their investigation.

With regard to composition, EDX point analyses (see [38]) of the surface crystallites observed in this work confirm the presence of La, Sr, Co and O without any foreign elements, which suggests that these structures are probably a decomposition product of LSC64. EDX results indicate a slightly higher amount of Sr than the bulk, which would suggest strontium oxide, SrO. However, the EDX excitation volume of approx. 1 μm diameter is much larger than the analyzed surface structures and thus the signal obtained on the small crystals is masked by the underlying bulk phase. An attempt to determine the composition of the crystallites by STEM analysis turned out to be equally unsuccessful.
Ninia et al. [52] analyzed the composition of crystallites formed on the surface of LSCF6428 after annealing at high temperatures in dry and humid atmospheres by Auger electron spectroscopy (AES) and low energy ion scattering (LEIS). The authors found strong segregation of strontium to the surface and concluded that the crystallites are Sr-based compounds. The exact composition of the crystallites (SrO, SrO$_2$, Sr(OH)$_2$, or SrCO$_3$) could not be unambiguously determined. Oh et al. [51] identified precipitates on LSCF6428 as a Sr-O compound, but could not pinpoint the exact composition (i.e., SrO or SrO$_2$) either. Results from nano-probe AES presented by Pişkin et al. [57] also suggest a Sr-O based makeup of particles formed on a LSCF6428 surface after high-temperature annealing.

With respect to the conditions applied in this study, a thermodynamic analysis of the Sr-O-H system [58] shows that at 700°C and 0.2 bar p$_{O_2}$ with 60% relative humidity (≈ 0.02 bar pH$_2$O) the equilibrium phase is clearly located within in the stability region of SrO, where a formation of the peroxide compound SrO$_2$ would require much higher oxygen partial pressures and significantly higher humidity levels would be necessary to form Sr(OH)$_2$. Investigations on La$_2$O$_3$ thin films showed that at temperatures above 700 K complete de-hydroxylation is attained [59]. Surface precipitation of SrO$_2$ was reported by Chen et al. [60] after annealing thin-film layers of the related Ruddlesden-Popper compound (La,Sr)$_2$CoO$_4$ at 500°C in oxygen without humidity. However, it is unclear whether the surface particles found in the present study, as well as those observed by other authors, correspond to equilibrium phases. Further uncertainties may arise from experimental difficulties in identifying the composition of surface species at the nanoscale level without interference of the bulk material.

Our results of microstructural investigations of the ancillary samples with screen-printed electrodes at intermediate stages of the degradation study (for details see [38]) confirm that the formation of the surface crystallites is certainly linked to humidity, since no patterning was found on the surface of electrodes annealed at 700°C in dry atmospheres. In the absence of any other irregularities it is concluded that a deactivation of the oxygen surface exchange process due to the compositional changes of the electrode surface is responsible for the degradation of the electrode, as has also been reported by many other groups (see, e.g., [61, 62]). This is also in agreement with results from EIS analysis (Figure 10, top left), showing that the main feature affected by the degradation driver is the mid-frequency process, usually ascribed to the overall electrode process involving the surface exchange of oxygen as a crucial step.

STEM-HAADF images of a cross section of the degraded spin-coated electrode are presented in Figure 12. A comparison with the as-prepared state (see Figure 2, top) shows a rougher and more uneven morphology, which might be due to restructuring or recrystallization processes in humid atmospheres. Chemical analyses were performed by STEM-EDX measurements on selected positions of the sample (for details see [38]). The results confirm the expected elements La, Sr and Co in the grains, whereas the porous regions of the thin-film structure contain significant amounts of Si and Pt. While Pt was introduced during focused ion beam (FIB) sample preparation, Si is a critical contaminant, which appears to have been deposited on the electrode during the long-term experiment. Si was also detected inside the bulk of the CGO electrolyte with its highest concentration near the electrode-electrolyte interface and decreasing concentration at greater depths, following a typical diffusion profile with a penetration depth of about 200 nm. These findings indicate that Si was deposited at the electrode and at the electrode-electrolyte interface and subsequently diffused into the dense CGO bulk. This is a strong indication that gas phase transport of silicon in humid atmospheres occurred during the long-term experiment, with the most likely Si source being the quartz glass reactor. The fact that Si is found preferably in the porous layers of the spin-coated electrode can be explained by the gas phase transport and deposition mechanisms [53, 56, 63] and the fact that Si readily forms silicate layers on the surface but does not diffuse into the bulk of the perovskite structure [55, 64]. Surface accumulation of silicate species clearly reduces the oxygen surface exchange activity of electrode materials and is thus assumed to be the main cause for the electrochemical degradation observed in this study, though separating its contribution from grain coarsening effects within the spin-coated layers is difficult.

Figure 13 (top left) shows a STEM-HAADF image of the cross section of an infiltrated electrode layer. Nanoscale
infiltrated LSC64-grains deposited on the inner surface of the porous CGO backbone are clearly visible. The backbone structure appears to be covered well by the infiltrated material and smaller pores are partially filled up by nano-grains (Figure 13, bottom row). A few grains consisting of secondary phases were found as well. Figure 13 (top right) shows a detailed view of a region in the degraded electrode where the CGO backbone phase (1), the infiltrated material LSC64 (2), and the secondary phase (3) are visible. EDX analyses on the labeled spots confirm this assignment and identify the secondary phase as a mixture of Sr, S and Cr with a Sr:S:Cr-ratio of about 50:40:10 at.%. It is assumed that this secondary phase is a solid phase as a mixture of Sr, S and Cr with a Sr:S:Cr-ratio of about 50:40:10 at.%. The top right picture shows a close-up of a pore in the CGO backbone (1), covered with infiltrated LSC64 particles (2) and filled with a Sr(Cr,S)O₄ impurity phase (3).

Fig. 13 STEM-HAADF (top row) and FE-SEM images in BSE mode (bottom row) of a cross-section of the degraded LSC64-infiltrated electrode layer as overview (top left) and at higher magnifications (bottom row). The top right picture shows a close-up of a pore in the CGO backbone (1), covered with infiltrated LSC64 particles (2) and filled with a Sr(Cr,S)O₄ impurity phase (3).

4 Conclusions

The results in this study clearly show that humidity is a crucial factor strongly enhancing degradation rates of LSC64 proposed as high-performance SOFC cathode material. Moreover, systematic EIS experiments with LSC64 model electrodes with three different architectures reveal that the long-term performance is strongly determined by the morphology and microstructure of the electrodes. Conventional electrode microstructures applied by screen-printing, which is a standard fabrication technique for SOFC cathodes, show only a moderate increase of the polarization resistance (0.03–0.06 Ω cm² kH⁻¹) at 700°C in humid atmospheres. Somewhat lower degradation rates are observed for nano-structured electrodes of LSC64 infiltrated in a CGO backbone, whereas spin-coated LSC64 electrodes are found to deteriorate significantly faster. The lower degradation rates of screen-printed and infiltrated electrodes might be explained by the large surface areas of these structures, which are due to high porosities and larger electrode thicknesses (screen-printed electrodes) or coating of porous scaffolds with nanoscale particles (infiltrated electrodes). The high surface area is thus not only beneficial for the prime purpose of the electrode – surface oxygen exchange between gas phase and electrode – but also entails a larger capacity for accommodating impurities deposited on the surface. The infiltrated electrode, which shows the highest stability in the long-term tests, has also the largest surface area. In addition, it contains a porous current collector layer on top, which might have acted as an additional protective layer by gettering contaminants from the gas phase (Cr, Si, SO₂, etc.) and thus protecting the active layer underneath. Following these assumptions, a general strategy to reduce the impact of poisoning on the long-term stability of SOFC cathodes could be the combination of an active infiltrated cathode layer and a rather thick porous getter layer with sufficient affinity towards potential impurity species.

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