Long-term stability of the IT-SOFC cathode materials $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$ against combined chromium and silicon poisoning

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Abstract

Long-term degradation effects of combined Cr- and Si-poisoning on the promising IT-SOFC cathode materials $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$ were investigated at 700°C in dry and humid atmospheres for subsequent periods of 1000 hours using dc-conductivity relaxation measurements. Degradation-induced changes in chemical composition and morphology of the contaminated sample surfaces were studied by atomic force microscopy, X-ray photoelectron spectroscopy and scanning electron microscopy with energy and wavelength dispersive X-ray analysis. Upon exposure to humid, Cr- and Si-containing gas flows both materials exhibit a strong decrease of the chemical surface exchange coefficient of oxygen by a factor 110 and 40 for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$, respectively, which can be attributed to the formation of Cr-containing crystallites on the degraded sample surfaces. Post-test analyses confirm large amounts of Cr accompanied by a Sr-enrichment within the first 600 nm of the surface of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, indicating the decomposition of the perovskite phase by $\text{SrCrO}_4$-formation. For $\text{La}_2\text{NiO}_{4+\delta}$ the penetration depth of chromium is significantly less and Cr-traces up to a depth of up to 140 nm were determined by depth profiling. For both compounds silicon was found to spread in small patches across the entire sample surface as determined by elemental mapping analysis.
1. Introduction

Solid oxide fuel cells (SOFCs) are high-temperature devices which offer highly-efficient and low-noise conversion of chemical to electrical energy. Due to the high operating temperatures (above 600°C) SOFCs can utilize a wide variety of fuels (H₂, CH₄, diesel reformate, biogas etc.) without the need for expensive noble metals as catalysts for electrode reactions or pre-reforming. While it appears that SOFC-technology has reached a high level of maturity with respect to performance and efficiency, long-term degradation remains one of the main technical barriers for market entry. Lifetimes of 5000-10,000 hours for mobile applications and 45,000-100,000 hours for stationary use are often cited as requirements needed for successful commercialization [1].

Many degradation phenomena take place at the cathode and its interface to the electrolyte. A well-known mode of degradation is chromium poisoning of the cathode by gas phase transport of volatile Cr-species released from Cr-containing metallic interconnects or balance-of-plant (BOP) components [2]. In the case of interconnects protective layers – either applied as a thin coating or developed in-situ through high-temperature scale formation – are used as a countermeasure but cannot completely suppress the emission of Cr-species into the gas phase [3,4]. Similar degradation issues may be caused by poisoning of the cathode with silicon species released into the gas stream from silicate-based glass sealing materials or heat-resistant alloys used in BOP-components [5-10].

Cathode poisoning by Cr- and Si-species is strongly depending on the level of humidity in the oxidant by enhancing the gas transport rates for both elements. This effect can be rationalized by thermodynamic considerations through the comparatively high equilibrium partial pressures of Si- and Cr-oxyhydrates. Humidity
in the gas stream is an essential pre-requisite for Si-transport at SOFC-operating temperatures since the volatility of SiO$_2$ and SiO is very low below 1000°C while the di-hydrate H$_4$SiO$_4$ is the primary gaseous Si-species under oxidizing conditions [11,12]. Chromium has relevant partial pressures in its highest (hexavalent) oxidation state, CrO$_3$ being the dominant gas species in dry and oxidizing conditions while the corresponding mono-hydrate H$_2$CrO$_4$ is more volatile in humid atmospheres [13].

Degradation mechanisms of Cr- and Si-poisoning proceed by deposition of Cr and Si-species at the triple phase boundaries as well as on the cathode surface in the electroactive region of the electrode, thus blocking active sites for the oxygen reduction reaction. Moreover, the deposited layers are often found to react with the underlying cathode material, forming electrically insulating reaction products and changing the local composition of the phase in the surface region [14-16].

On this latter point Sr appears to play an important role, since it is used as a substituent in many cathode materials and has often been observed in reaction phases like Sr-silicates [11,17,18] and SrCrO$_4$ [2,19]. Judging from thermodynamic stabilities calcium and barium are expected to have a similar tendency to chromate formation [20]. Thus it appears to be worthwhile to investigate alkaline earth-free cathode materials with regard to their resistance to Cr- and Si-poisoning. A positive example of this approach is LaNi$_{0.6}$Fe$_{0.4}$O$_3$, which has been proposed in the literature as a SOFC-cathode material with high Cr-tolerance [21-23].

In this work a comparative study about the long-term effects of Cr- and Si-poisoning on the stability of the highly active Sr-containing perowskite compound La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC) and the promising Sr-free material La$_2$NiO$_{4+\delta}$ (LNO) was conducted. In the course of the degradation experiment the samples were exposed to increasingly harsh conditions with respect to humidity and Si/Cr-content in the atmosphere.
Since poisoning phenomena will proceed from the material surface, degradation processes were characterized on the basis of the temporal evolution of the chemical surface exchange coefficient of oxygen \((k_{\text{chem}})\), which is considered a representative parameter reflecting the state of the cathode surface. In addition to being a fundamental quantity to characterize the performance of mixed ionic-electronically conducting compounds for SOFC and membrane applications [24,25], \(k_{\text{chem}}\) is known to be very sensitive to surface modifications and thus can be used to continuously monitor \textit{in-situ} the progress of surface degradation over extended periods of time.

To gain more insight into the type of surface modification and degradation mechanism, samples at different stages in the degradation process were analysed employing various surface sensitive techniques. EDXS-elemental mappings from scanning electron microscopy provided large-area information about the lateral distribution of constituents and contaminants on the surface. Particular topographical features of the surface were investigated in detail by atomic force microscopy (AFM) and elemental depth profiles of the surface zone were obtained by X-ray photoelectron spectroscopy (XPS) combined with Ar-sputtering.

2. Experimental

2.1 Sample preparation

Commercial powders of LSC (EMPA, Dübendorf, Switzerland) and LNO (Treibacher Industrie AG, Althofen, Austria) were isostatically pressed into cylindrical pellets at 250 MPa and 200 MPa, respectively. LSC was sintered once for 10 hours
at 1200°C in air and LNO twice for 10 hours at 1350°C in air with heating and cooling rates of 2 Kmin\(^{-1}\) to obtain tablets with relative densities of above 95%. Thin squares of approximately 6×6 mm\(^2\) were cut from the sintered tablets with a diamond wire saw. The thin slices of LSC and LNO were ground with a diamond grinding disk and polished by means of polymer-embedded diamond lapping films with 30, 6 and 1 µm particle size to a final thickness of 519 µm and 412 µm, respectively. Gold wires were attached to the corners of the square samples to establish electrical contacts using gold paste (Metalor).

2.2 Electrical conductivity relaxation measurements

To investigate the oxygen exchange kinetics four point dc-conductivity relaxation experiments were conducted at 700°C in van der Pauw electrode configuration [26]. The experiments were performed in a quartz glass reactor that served as a constant silicon source in humidified atmosphere. Oxidation and reduction steps were applied by changing the oxygen partial pressure in the vicinity of the sample abruptly between \(1.0 \times 10^{-1} \leq p(O_2)/\text{bar} \leq 1.5 \times 10^{-1}\) using dry and humidified \(O_2\)-Ar gas mixtures at a constant flow rate of 2 dm\(^3\) h\(^{-1}\). Humidification of the test gases was realized by passing the gas streams through gas washing bottles which were filled with deionized water and placed into a thermostat. To achieve relative humidities (r.h.) of 30% and 60%, the thermostat was set to 6°C and 17°C, respectively. A constant current of 200-400 mA was applied to the samples and the voltage response was recorded as a function of time. The chemical surface exchange coefficient \(k_{chem}\) and the chemical diffusion coefficient \(D_{chem}\) of oxygen were obtained from the conductivity relaxation data using non-linear regression of the corresponding solutions of the diffusion equation [27,28]. The effects of chromium poisoning were
simulated by placing a chromium pellet upstream close to the specimen thus exposing the sample to chromia-containing gas flows. A more detailed description of the experimental procedure is given elsewhere [29].

2.3 Atomic force microscopy

Topography images were recorded with an Asylum Research MFP-3D atomic force microscope (AFM), equipped with a planar closed loop scanner. The AFM was operated in tapping mode at a set-point-to-free amplitude ratio of 0.8. Olympus OMCL-AC160TS silicon probes with a typical spring constant of $k = 42 \text{ Nm}^{-1}$ were used to scan the surface of the samples. The probes had a tetrahedral tip with an opening angle of approximately $35^\circ$ and a nominal tip radius of 7 nm. The root mean square surface roughness $\sigma_{\text{RMS}}$, which describes the root mean square deviations of the height level of the analyzed surface from the average height level, was calculated from topographical data according to

$$\sigma_{\text{RMS}} = \sqrt{\frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} (z(x_i, y_j) - \mu)^2}$$

(1)

where $x$, $y$ and $z$ denote the image coordinates, $\mu$ the average height level and $N$ the resolution of the image in $x$- and $y$-direction [30].

2.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Perkin Elmer PHI 5600 ESCA system with a hemispherical analyzer in the constant analyzer mode. A standard X-ray source was used to record the spectra with Mg-Kα
radiation (1253.6 eV). The analyzed area was restricted to a spot with a diameter of 400 µm by the Omnifocus lens. Survey scans at a pass energy of 93.9 eV were conducted to check for potential unknown contaminants prior to depth profiling. A 10 kV Ar\(^+\) ion beam with a diameter of approximately 150 µm was applied for depth profiling. An Atomica WF 421 Microfocus Ion Gun was used to automatically scan a sample area of 1.2×1.5 mm\(^2\), irradiating the surface at an ion current of 125 nA. A sputter rate was estimated by assuming a yield of 2 target atoms per impinging Ar\(^+\), considering the volume density of the bulk composition. It should be mentioned that with different sample compositions the sputter rates may deviate by a factor of 2. Despite the limitations of the present method, it is still possible to extract information about degradation induced changes in the surface elemental composition. A Shirley background function was applied for the background subtraction. Subsequently, the concentrations of the specific elements could be obtained from the core-level peak areas using standard relative sensitivity factors. The reproducibility of the XPS quantification is about 1%.

2.5 Scanning electron microscopy – energy dispersive X-ray spectroscopy

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDXS) analyses of LSC were performed using a Zeiss Ultra 55 microscope with an EDAX Phoenix detector for energy dispersive X-ray spectroscopy at acceleration voltages of 12 kV. Elemental distribution maps of LNO were recorded at acceleration voltages of 10 kV using a FEI Quanta 200 microscope with an EDAX Genesis detector for EDXS. High resolution images of LSC and LNO were recorded in secondary electron (SE) and backscattered electron (BSE) mode at acceleration voltages of 5 kV.
3. Results and discussion

3.1 Oxygen exchange kinetics

Results of electrical conductivity relaxation measurements over a period of about 3500 hours are illustrated in Figs. 1 and 2. For LSC both the chemical surface exchange coefficient $k_{chem}$ of oxygen and the chemical diffusion coefficient $D_{chem}$ of oxygen could be determined simultaneously, indicating mixed-controlled kinetics. For the LNO sample, however, only $k_{chem}$ was obtained because the kinetics is surface-exchange controlled [31,32].

In Fig. 1 results for $k_{chem}$ of LSC (a) and of LNO (b) are presented as a function of time at 700°C. At an oxygen partial pressure of $p(O_2) = 0.1$ bar both samples showed high initial $k_{chem}$-values of $1.1 \times 10^{-3}$ cm s$^{-1}$ (LSC) and $3.6 \times 10^{-4}$ cm s$^{-1}$ (LNO). The first 200–300 hours were performed without any chromium source to check for the intrinsic stability of the materials. Both samples show fairly stable surface exchange kinetics in the absence of chromium, thus indicating negligible intrinsic degradation. During the following 1000 hours the samples were exposed to a Cr- and Si-source in dry gas flow. For LSC, no Cr- and Si-induced degradation was observed under dry conditions. Post-test analyses of the sample revealed that deposited Cr and Si amounts, if present, were below the XPS detection limit after treatment in dry atmospheres (see section 3.3). In comparison, $k_{chem}$ of LNO decreases by a factor of 2.8. Subsequent XPS analyses confirm the presence of Cr-species on the surface within a layer of about 30 nm thickness. After the introduction of moderate humidity (30% r.h.), a pronounced decrease of $k_{chem}$ by a factor of 110 and 40 was observed.
for LSC and LNO, respectively. As will be discussed in section 3.2, the decrease of $k_{chem}$ can be attributed to Cr-induced changes of the surface morphology and phase decompositions in the surface-near regions. In addition, the deposition of poorly conducting Si-species released from the quartz glass reactor in humid atmospheres contribute to the deterioration of the surface exchange reaction. After exposure to increased levels of humidity (60% r.h.) the total decrease of $k_{chem}$ amounts to a factor of 250 and 230 for LSC and LNO, respectively. The increase in humidity does not accelerate the degradation rate, which is not surprising when considering the actual changes in partial pressure of the most abundant volatile Cr-species and Si-species released in humid atmospheres. At 700°C and a $p(O_2)$ of 0.1 bar the change in partial pressure of chromic acid ($H_2CrO_4$) from $5.4 \times 10^{-8}$ bar (30% r.h.) to $1.1 \times 10^{-7}$ bar (60% r.h.) is relatively small (partial pressures were calculated with FactSage v.6.4 based on data by Ebbinghaus [33]). Similarly, the partial pressure of $H_4SiO_4$ increases from $3.1 \times 10^{-11}$ bar (30% r.h.) to $1.3 \times 10^{-10}$ bar (calculations based on data from Jacobson et al. [34]).

In the case of LSC, the simultaneous determination of surface exchange coefficients and chemical diffusion coefficients was possible. The initial value for $D_{chem}$ of $4.7 \times 10^{-6}$ cm$^2$s$^{-1}$ remained constant during exposure to Cr-containing atmospheres without humidification. Once humidity was added to the gas stream, $D_{chem}$ started to decrease. Over the entire duration of the experiment $D_{chem}$ dropped by a factor of 65 which can probably be ascribed to the formation a relatively thick layer of Cr-containing compounds on the sample surface which exhibits a much smaller $D_{chem}$ compared to the bulk phase. A similar behaviour was also observed in a previous study [18].

3.2 Atomic force microscopy
In order to examine degradation-induced changes in the surface morphology pre- and post-test analyses of LSC and LNO samples were performed using AFM. Figs. 3 and 4 present large area surface scans (10×10 μm²) of LSC and LNO of (a) the fresh, polished surface, (b) after 1000 h in a dry atmosphere in the presence of chromium and silicon, (c) after an additional 1000 h of exposure to a Cr- and Si-source in a moderately humidified atmosphere (30% r.h.) and (d) after further 1000 h of exposure to a Cr- and Si-source in a strongly humidified atmosphere (60% r.h.).

The fresh LSC sample depicted in Fig. 3a shows fine scratches caused by the polishing procedure. Small cavities from residual porosity with a maximum depth of approx. 200 nm can be observed in some regions. In other areas shallow, irregularly structured craters are visible which result in a relatively high surface roughness for a polished surface (\(\sigma_{\text{RMS}} = 47.5\) nm). In direct comparison the LNO sample features a relatively smooth surface (\(\sigma_{\text{RMS}} = 3.3\) nm) (Fig. 4a).

After 1000 h of exposure to Cr and Si in a dry atmosphere the surface roughness of LSC is increased by a factor of 2.5 (\(\sigma_{\text{RMS}} = 122.8\) nm), indicating an increase in the number of surface features. The AFM-image (Fig. 3b) reveals sharp-edged craters and small crystallites in the initial phase (early state of growth) with a size of approximately 200 nm protruding from the surface. For the LNO sample (Fig. 4b) the surface roughness (\(\sigma_{\text{RMS}} = 18.1\) nm) likewise increases after 1000 h in dry Cr- and Si-containing atmospheres and the surface features small rod-like crystallites. Some areas show cavities of approximately 1 μm diameter which are surrounded by a cluster of crystals along their circumference.

Fig. 3c shows the LSC surface after an additional 1000 h at 30% r.h. The surface is covered with faceted crystals of 0.15-2 μm diameter and up to 450 nm height. Furthermore, the surface roughness increased by a factor of 1.5 (\(\sigma_{\text{RMS}} =


172.6 nm. Compared to the rather coarse crystallites formed on the LSC surface, the AFM image of LNO (Fig. 4c) reveals a surface that is densely covered with small round grains ($\sigma_{\text{RMS}} = 34.2$ nm).

Exposure of the sample to 60% r.h. over the course of another 1000 hours resulted in promoted crystal growth which is illustrated in Figs. 3d and 4d, resulting in a decrease of surface roughness ($\sigma_{\text{RMS}} = 136.2$ nm). The crystals found on the LSC sample surface bear a resemblance to truncated pyramids in different sizes with squared and rectangular bases (see also Fig. 5a), whereas the surface of LNO ($\sigma_{\text{RMS}} = 31.7$ nm) is covered with round protrusions of irregular shape and size (Fig. 5b).

### 3.3 X-ray photoelectron spectroscopy

For the analytical investigation of the surface composition along different stages in the degradation process XPS depth profiles were recorded after 1000 hours at 700°C in a dry gas flow of 10% O$_2$/Ar with a Cr- and Si-source, after additional 1000 hours in a moderately humidified (30% r.h.) gas stream and after further 1000 hours under strongly humidified conditions (60% r.h.). Depth profiles of freshly polished, non-degraded samples were recorded for comparison. XPS-profiling was extended to sputtering depths where a constant bulk composition was reached. It should be mentioned that due to preferential sputtering of lighter elements by the Ar-beam the measured bulk compositions are deviating from the nominal compositions of the investigated materials. Nevertheless, the method provides general trends regarding changes in surface composition among different samples.

In Fig. 6a the elemental depth profiles of the non-degraded LSC sample are depicted, confirming a homogenous composition within the first 200 nm of the sample. Abrupt changes in the topmost layer are an artifact originating from carbon
or hydrate/hydroxyl species adsorbed at the surface [18]. Indeed, significant amounts of carbon have been detected by XPS before the first sputtering step but are omitted from the profiles in Figs. 6 and 7 for reasons of clarity. After exposing LSC for 1000 hours to Cr and Si under dry conditions, a significant enrichment of Sr within the first 100 nm is detected (Fig. 6b). Trace amounts (usually < 3 at.%) of Bi (on LSC) and Bi and Cd (on LNO) originating from the contacting gold-paste were found within the topmost surface layer (not shown in Figs. 6 and 7). Potentially deposited amounts of Cr and Si are below the detection limit of the method. In comparison, the depth analysis of LNO reveals the deposition of small amounts of Cr even under dry conditions (Fig. 7b), in agreement with the observed decrease of $k_{chem}$ in dry atmospheres as discussed in section 3.1. Moreover, the data indicates a slight increase of La/Ni-ratio within a surface zone of 40 nm. Depth profiles of the LSC sample annealed in 30% r.h. (Fig. 6c) confirm the presence of Cr up to a depth of 600 nm. Large amounts of Cr were detected within the first 200 nm of the sample surface, accompanied by Sr-enrichment and depletion of La and Co. XPS-analysis of the LNO surface (Fig. 7c) shows a significantly lower concentration of Cr than the LSC sample. Cr is found up to depths of 140 nm. Also, La-enrichment and Ni-depletion are more pronounced than after treatment in dry atmosphere. Fig. 6d shows the LSC sample after additional 1000 hours under strongly humidified conditions (60% r.h.). The data indicate a Cr-contamination up to depths of more than 700 nm and a Sr-enriched and La/Co-depleted zone of several 100 nm. In comparison, the Cr-poisoned surface layer of LNO (Fig. 7d) is much thinner (around 140 nm) and contains lower amounts of Cr.

3.4 Scanning electron microscopy
After the long-term oxygen exchange experiments SEM-EDXS analyses were performed on the strongly degraded samples to gain further information about modifications of the sample surface. Fig. 8 shows the BSE image of a section of the degraded surface of LSC, as well as the corresponding elemental distribution maps of La, Sr, Co, O, Si and Cr. Dark areas in the images of La and Co coincide with brighter areas in the maps of O and Cr, which agrees well with trends observed in the XPS-profiles. Some Sr-rich areas appear to be depleted of La and Co, but enriched with Cr. This could be evidence of the formation of SrCrO$_4$ which was also reported in similar Cr-poisoned SOFC cathode materials [3,35,36]. However, the resolution of EDXS is too low to determine the actual composition in this area reliably. Moreover, it should be mentioned that the Cr-L peak (0.573 eV) is overlapping with the O-K peak (0.523 eV) which limits the accuracy of quantification for both Cr and O. Si is distributed over the entire surface and was confirmed separately by WDXS. Preliminary TEM-results of surface regions on degraded LSC give further evidence of the formation of SrCrO$_4$ and will be dealt with in a forthcoming publication.

In Fig. 9 the SEM-BSE image and the elemental distribution maps of degraded LNO are presented. The BSE image shows individual grains which are visible due to channelling contrast, as well as some isolated particles on top of the surface. Small dark spots coincide with bright areas in the Ni-map and correspond to NiO-inclusions. NiO has also been detected on a fresh sintered sample obtained from the same tablet used for the preparation of the LNO sample and thus originates either from impurities in the raw powder or is formed during sintering. However, room temperature X-ray diffraction (XRD) measurements indicate that NiO is not present in the raw powder (pattern not shown). La and O seem to be homogenously distributed over the entire surface. Si was also confirmed and found to be spread in concentrated patches across the entire surface. The quantification of Cr by EDXS-
mapping turned out to be unreliable due to the strong overlap of Cr-peaks with lines of O and La. In addition, the amounts of Cr on degraded LNO determined by XPS-measurements are significantly smaller than for LSC (see section 3.3).

4. Conclusions

The long-term stability against simultaneous Cr- and Si-poisoning of the promising IT-SOFC cathode materials La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ (LSC) and La$_2$NiO$_{4+δ}$ (LNO) was investigated at 700°C in dry and humidified O$_2$/Ar gas streams for more than 3000 hours using dc-conductivity relaxation experiments. The chemical surface exchange coefficient ($k_{chem}$) and the chemical diffusion coefficient ($D_{chem}$) of oxygen were determined as a function of time to monitor the degradation process. At different stages of the experiment AFM-images of the sample surface were recorded and XPS-depth profiles were measured. In addition, elemental distribution maps of the fully degraded sample were obtained using SEM-EDXS. The results of the long-term stability measurements show that both materials exhibit excellent stability under dry, Cr-free conditions. In the presence of a Cr- and Si-source LSC and LNO are fairly stable under dry conditions for a time period of 1000 hours. LNO shows a slight decrease in $k_{chem}$ which can be attributed to small quantities of Cr deposited on the surface as confirmed by XPS. However, after humidification of the gas stream, both compounds experience a severe degradation of the surface exchange reaction, with LSC being affected slightly stronger than LNO. AFM images show the formation of a relatively thick surface layer of large crystals on LSC. In comparison, the Sr-free material LNO forms significantly smaller crystals which also appear to contain less Cr as shown by XPS. It can therefore be concluded that LSC seems to be more
susceptible towards Cr-poisoning in humidified atmosphere than LNO. However, the absence of Sr in LNO does not prevent Cr-induced degradation. Volatile Si-species released from the quartz glass reactor and deposited on the surface additionally contribute to the decline of the surface exchange rate. Experiments in this work thus simulate the conditions encountered in real SOFC-systems where both Cr- and Si-contaminants are present simultaneously in the gas phase of the cathode side. Deterioration by Cr- and Si-poisoning is significantly enhanced in humid atmospheres due to increased gas phase transport of volatile Cr- and Si-compounds. Hence, it can be concluded that maintaining dry operating conditions by e.g. pre-drying of the oxidant flow is beneficial for improving long-term stability of SOFC-cathodes.

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References


Figure captions

**Fig. 1.** Chemical surface exchange coefficients of oxygen for LSC (a) and LNO (b) at 700°C and \( p(O_2) = 0.1 \) bar as a function of time. A silicon source was present for the entire duration of the experiment. Chromium was introduced after approximately 300 hours.

**Fig. 2.** Chemical diffusion coefficient of oxygen of LSC at 700°C as a function of time. A silicon source was present for the entire duration of the experiment. Chromium was introduced after approximately 300 hours.

**Fig. 3.** Surface morphology of different LSC samples; AFM scans (10×10 µm²) of (a) the fresh, polished surface, (b) after 1000 h in dry atmospheres in presence of a Cr- and Si-source, (c) after an additional 1000 h of exposure to a Cr- and Si-source in a moderately humidified atmosphere (30% r.h.) and (d) after a further 1000 h with Cr and Si in a strongly humidified atmosphere (60% r.h.).
**Fig. 4.** Surface morphology of different LNO samples; AFM scans (10×10 µm²) of (a) the fresh, polished surface, (b) after 1000 h in a dry atmosphere in presence of a Cr- and Si-source, (c) after an additional 1000 h of exposure to a Cr- and Si-source in a moderately humidified atmosphere (30% r.h.) and (d) after a further 1000 h with Cr and Si in a strongly humidified atmosphere (60% r.h.).

**Fig. 5.** Comparison of surface structures of degraded LSC and LNO samples; high resolution AFM images (1×1 µm²) of (a) LSC and (b) LNO after 3000 h in dry and humid atmospheres in close proximity to a Cr-pellet and a Si-source.

**Fig. 6.** XPS elemental depth profiles of La, Sr, Co and O in LSC and Cr-impurities in (a) the fresh sample, (b) after 1000 h of exposure to a dry atmosphere in the presence of a Cr- and Si-source at 700°C, (c) after an additional 1000 h of exposure to a Cr- and Si-source in a moderately humidified atmosphere (30% r.h.) and (d) after a further 1000 h in vicinity to a Cr-pellet and Si-source in a strongly humidified atmosphere (60% r.h.).
Fig. 7. XPS elemental depth profiles of La, Ni and O in LNO and Cr-impurities in (a) the fresh sample, (b) after 1000 h of exposure to a dry atmosphere in the presence of a Cr- and Si-source at 700°C, (c) after an additional 1000 h of exposure to a Cr- and Si-source in a moderately humidified atmosphere (30% r.h.) and (d) after a further 1000 h in vicinity to a Cr-pellet and Si-source in a strongly humidified atmosphere (60% r.h.).

Fig. 8. Post-test SEM-BSE image (top left) and SEM-EDXS elemental distribution maps of the degraded LSC sample; the Si-map was acquired by SEM-WDXS.

Fig. 9. Post-test SEM-BSE image (top left) and SEM-EDXS elemental distribution maps of the degraded LNO sample.
Figure 1.
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