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The influence of LSCF sintering atmosphere on the formation of impurity phases and stack performance

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Abstract

The perovskite material $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) is frequently used as air electrode material in fuel electrode-supported solid oxide cells (SOC) [1]. While the high temperature sintering of the electrode material during cell manufacturing is inevitable to achieve competitive cell and stack performance, it is also a driving force for the formation of detrimental impurity phases at the electrode/electrolyte interface, e.g. SrZrO_3 [2]. The formation of interface impurities can be reduced, but often not fully inhibited, by applying a barrier layer of Gd doped CeO_2 (GDC) between the LSCF electrode and the electrolyte made of yttria-stabilized ZrO_2 (YSZ).

Therefore, we investigate in this study, if using dry synthetic air as sintering atmosphere for the LSCF electrode can further reduce the formation of impurity phases or influence the Sr outward diffusion from the lattice and hence improve the cell performance. To achieve well comparable results stack-size relevant cells were manufactured with air-electrodes sintered in dry synthetic air or ambient air. Subsequently, a “rainbow” stack with cells sintered in dry or ambient air was assembled and operated. In order to get an insight into the influence of the sintering conditions on the electrode itself as well as on the electrode/electrolyte interface a detailed post-test analysis of the microstructure, crystallinity, and elemental composition is conducted. Among other analytical techniques, scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDS) is used to investigate the microstructure and elemental composition. The structural properties are analyzed by X-ray diffraction (XRD) and Raman spectroscopy. By performing these characterizations on pristine cells as well as on cells used in industry relevant stack testing experiments, it should be possible to distinguish between processing effects and degradation effects occurring during stack testing.

Introduction

Solid oxide cells (SOC) are a key technology for the efficient and sustainable utilization of hydrogen in the ongoing energy transition [3]. Although, on the path to a wide market entry of SOC there are still some bottlenecks to be solved, like for example the general reliability and the performance decay over time. Both of these parameters can be drastically influenced by the manufacturing process of the cell components. One critical aspect in the manufacturing of fuel electrode-supported SOC via a conventional, industrially scalable ceramic processing route are the essential high sintering temperatures. While these high temperatures are indispensable to form a well-established connection between the different layers in the cell (e.g. GDC barrier and LSCF air electrode), the high temperatures are also a driving force for the formation of unwanted impurity phases. One of these well-known impurity phases with negative impact on the cell performance is SrZrO_3 that is formed due to the reaction of mobile Sr from the LSCF air electrode with the YSZ electrolyte. The physical separation of LSCF and YSZ with a barrier layer (e.g. GDC) can already drastically inhibit the formation of SrZrO_3 , but in general, it cannot be fully suppressed [2].

1. Scientific Approach

In literature it has been shown that SrZrO_3 is already formed when LSCF and YSZ are only put in close proximity without any direct physical contact [4]. This indicates that the Sr transport at elevated temperatures during cell manufacturing and hence the formation of SrZrO_3 is at least to some extent proceeding via gas phase transport of volatile Sr containing species. Furthermore, it has been reported that among the volatile Sr species $\text{Sr}(\text{OH})_2$ has the highest partial pressure in the temperature region relevant for cell processing with a direct correlation to humidity [4,5]. Thus, it is concluded in literature that the gas phase transport of segregate SrO from the LSCF surface is highly facilitated by air moisture [4,5].

In this study the potential impact of air moisture during LSCF sintering in an industrially relevant cell manufacturing process has been analyzed. In order to do so, the LSCF cathodes of application relevant SOC have been sintered in dry synthetic air (79% N_2 , 21% O_2) and in ambient air.

2. Experiments

A 6-plane stack in the so called Jülich F-design [6] was assembled by stacking six fuel-electrode supported cells (100x100 mm²) with conventionally or dry air sintered LSCF electrodes in an alternating sequence. The stack was afterwards tested in fuel cell mode at 700 °C for ~1000 h with a load of 0.5 A cm⁻². After the stack testing the stack was disassembled and the different cells were subjected to a detailed post-test analysis. In order to better distinguish between effects originating from the manufacturing process or from the stack operation, additional reference cells with LSCF electrodes sintered in dry or conventional air but without any electrochemical testing history have been analyzed in parallel. All cells have been stored in a desiccator until needed for stack assembling or characterization to reduce contact with air moisture prior to the stack testing or characterization

The quantitative elemental composition of the cells was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES), considering besides the major constituent elements of the cell also impurity elements and elements originating from stack operation like e.g. Cr, Al. The overall crystal structure of the materials was investigated by XRD measurements at different incident angles. The microstructural properties have been

investigated by scanning electron microscopy in combination with energy dispersive X-ray spectroscopy to get also localized information on elemental composition.

3. Results and Discussion

Figure 1 shows the initial I-V curves at three different temperatures, as well as I-V curves at 701 °C before and after operation for ~1000 h (inset, Figure 1). For reasons of clarity only two out of the six layers are exemplarily shown in this graph. Except of layer 1, which had an issue with the contacting within the stack, all the other layers showed a very similar behavior in the I-V measurements. As can be seen in the plotted data, there is no big difference visible when comparing the cell with LSCF sintered in ambient air to a cell with LSCF sintered in dry air. Neither prior to operation, nor after about 1000 h at 700 °C with a load of 0.5 A cm⁻². The overall degradation of the different cells (except for layer 1) is slightly in favor for the dry air sintered LSCF cells with values ranging from 2.5 to 3.6 mV kh⁻¹ compared to 4.1 and 3.1 mV kh⁻¹ for the cells with LSCF electrode sintered in ambient air.

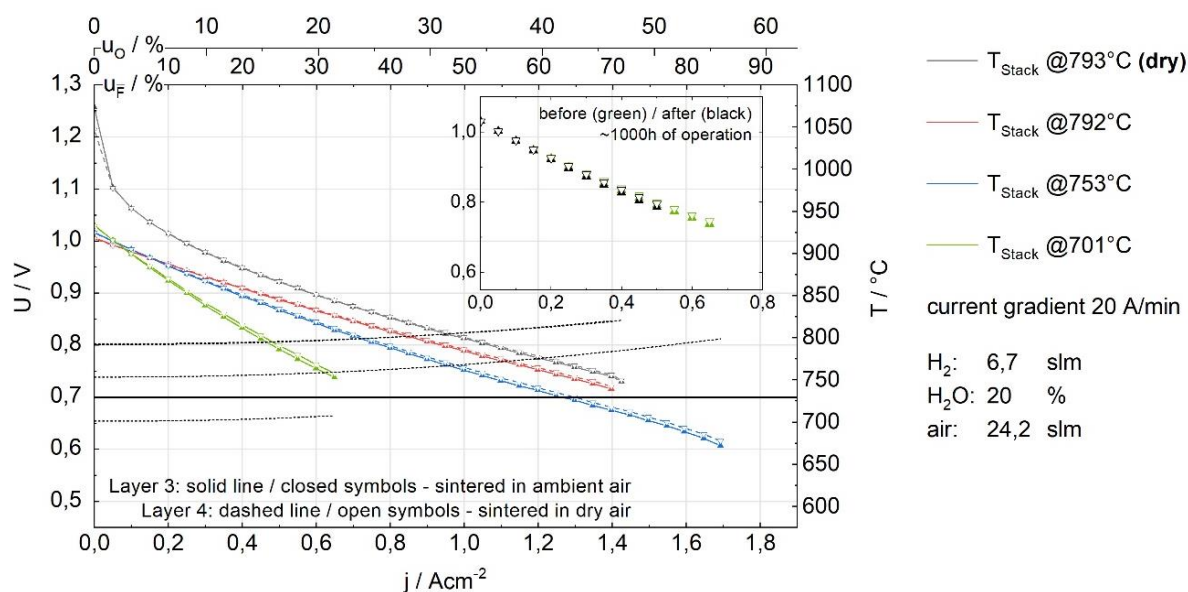


Figure 1: I-V curves at various stack temperatures (T_{Stack}). Inset shows I-V curves at $T_{\text{Stack}}=700$ °C before and after ~1000 h under load.

Wet chemical analysis

Table 1: Concentrations and cation ratios for LSCF elements calculated from ICP-OES analysis. Samples from four layers of the operated fuel cell stack and from the reference cells are listed.

Sample	La mg/cm ²	Sr mg/cm ²	La/Sr	Co mg/cm ²	Fe mg/cm ²	Co/Fe
Layer 2 (dry)	5,97	2,49	1,510	0,88	3,20	0,259
Layer 3 (ambient)	6,17	2,56	1,520	0,90	3,30	0,257
Layer 4 (dry)	6,35	2,65	1,511	0,92	3,36	0,260
Layer 5 (ambient)	5,42	2,26	1,514	0,79	2,90	0,258
ambient reference	4,54	1,91	1,498	0,66	2,41	0,260
dry reference	3,94	1,67	1,487	0,58	2,12	0,258

Table 1 summarizes the LSCF composition and cationic ratios for samples taken from four different cells used in the fuel cell stack testing and for samples from the pristine reference cells. The difference in the absolute values when comparing the samples from the stack test and the references cells can be explained by the additional LSCF cathode contact layer

(CCL) that was applied on the cells for the stack testing. After stack disassembling this CCL is still partially remaining on the cathode surface. Taking a look at the cation ratio, it can be concluded that in case of the Co/Fe ratio there is no real difference detected with respect to the sintering atmosphere and the measured values are close to the expected stoichiometric ratio of 0.25. In contrast, the La/Sr ratios show a slight Sr deficiency when compared to the expected stoichiometric ratio of 1.45. This might be an indication for an overall loss of Sr during sintering which is again slightly enhanced after cell operation. But with respect to the different sintering atmosphere in ambient and dry air there is no real trend in the measured La/Sr ratios detected.

For the measured impurity elements like for example Cr there was no significant increase detected when comparing the cells after the relatively short operation time of ~1000 h with the pristine reference cells.

Crystal Structure

Figure 2 represents XRD measurements in Bragg Brentano geometry taken from samples after stack testing (Figure 2, top) as well as from samples from the reference cells (Figure 2, bottom). Overall, the X-ray diffraction patterns for all samples can be clearly indexed with an LSCF reference pattern. Neither in the samples from the post-test characterization nor in the samples taken from the reference cell there is an obvious difference visible between samples with dry or ambient air sintering of the LSCF electrodes. The XRD also shows no impurity phases, but with respect to the expected SrZrO_3 at the GDC/YSZ interface, this should be due to the overall thickness of the LSCF air electrodes and the partially remaining CCL. Furthermore, when directly comparing the samples from post-test characterization with the reference samples the additional LSCF cathode contact layer of the post-test samples has also to be taken into account. The CCL is applied by screen printing on the LSCF electrode surface and the only heat treatment for this layer is the elevated temperature during stack formation and operation. This is also reflected in the XRD pattern by the relatively broader peaks in comparison to the peaks of the well crystallized LSCF electrode surface in case of the reference samples.

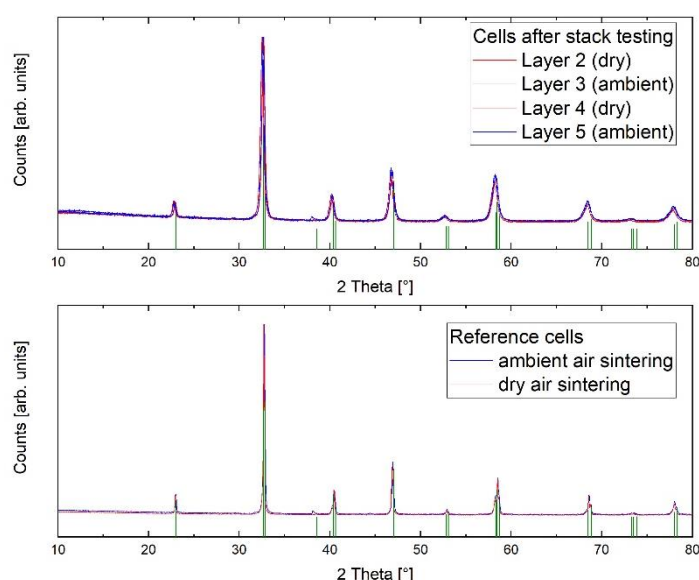


Figure 2: XRD patterns for samples from stack testing (top) and for samples taken from reference cells (bottom). LSCF reference pattern is indexed in green.

Microstructure Analysis

The surface microstructure for LSCF air electrodes sintered in ambient or dry technical air is exemplarily shown in the SEM images of Figure 3. These SEM images were taken on the reference cells, which show the pristine surface structure without any testing history or additional cathode contact layer on top. Both surfaces show well interconnected LSCF particles after the high temperature sintering process and a qualitatively similar porosity. Furthermore, in both cases there are finer additional particle structures visible that agglomerate mostly along grain boundaries. Unfortunately, these fine structure particles were too small to be independently analyzed by EDS without getting also a signal from the surrounding material. In the direct comparison of the ambient and dry air sintered sample the particles of the dry air sintered samples tend to be slightly larger in size. Multiple point analysis of both samples surfaces by EDS also revealed that there are some localized spots with an enriched Co-signal and a reduced Sr-signal, up to regions where almost no Sr can be detected. This tends to be a general processing artefact from the powder and does not originate from the different sintering atmosphere, because it was observed for both samples.

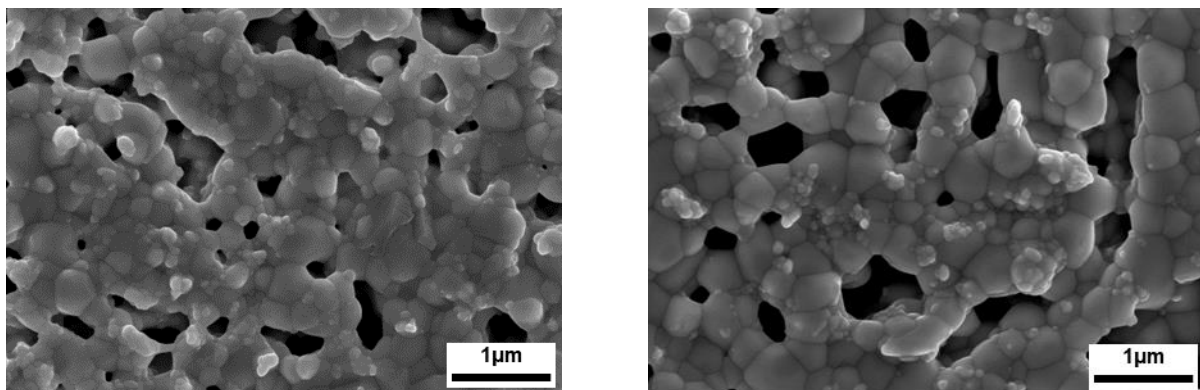


Figure 3: SEM images of the LSCF surfaces for the reference cell sintered in ambient air (left) and in dry synthetic air (right).

Figure 4 summarizes fracture surface images of the ambient and dry air sintered reference samples. As can be seen in both overview images, a fracturing parallel through the GDC barrier results in a slightly lower sample height for the LSCF electrode and parts of the GDC barrier layer. When focusing on the GDC/YSZ interface both samples show the formation of SrZrO_3 impurity phases which is visible by regions with darker contrast compared to the surrounding GDC. Qualitatively, there is no major difference observable in the SrZrO_3 distribution along the interface of the ambient or dry air sintered reference sample. These results indicate that during the sintering process the mobility of Sr via gas phase transport and via grain boundary diffusion is still sufficiently high and that solely the avoidance of air moisture cannot drastically change the SrZrO_3 formation at the GDC/YSZ interface.

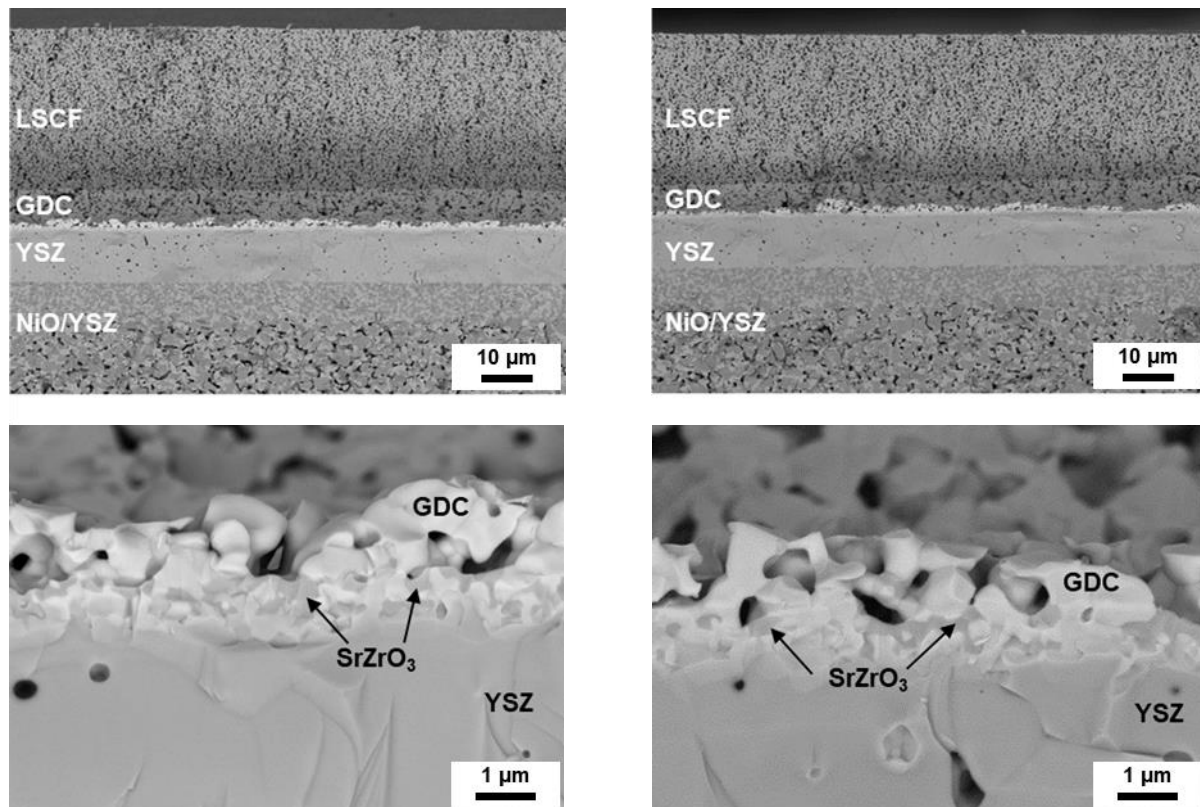


Figure 4: SEM images of fracture Surfaces for the reference cell sintered in ambient atmosphere (left) and in dry synthetic air (right).

4. Conclusion

Overall we come to the conclusion that sintering the LSCF air electrodes in either ambient air or in dry synthetic air does not affect the LSCF properties on a macroscopic scale and hence on the application relevant level. This is also reflected in the stack testing results that show nearly the same performance for the cells with LSCF electrodes sintered in ambient air and in dry synthetic air. Qualitatively, there is no major difference visible in the formation of possible impurity phases, e.g. SrZrO_3 .

References

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