

High Performance (La,Sr)(Co,Fe)O₃ Cathodes With Improved Adherence for Metal-Supported Fuel Cells

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A novel sintering approach was developed in order to overcome the issue of insufficient adherence of (La,Sr)(Co,Fe)O₃ type cathodes in metal-supported solid oxide fuel cells (MSCs). Investigation of the phase stability of the perovskite structure at high temperature in various atmospheres with low oxygen partial pressures provided the basis for the development of a specific sintering procedure. After detailed investigation of the layer adherence, time dependent mechanical integrity and reversibility of phase transformations, metal-supported cells with cathodes sintered before cell operation (ex-situ sintering) could be produced reliably and were electrochemically characterized in single cell measurements. The novel sintering approach of such cathodes resulted in a significantly enhanced mechanical stability of the cathode layers. The adherence of the cathode to the electrolyte was considerably stronger, which is a substantial improvement in comparison with state-of-the-art MSCs. Furthermore, the electrochemical measurements revealed a beneficial effect regarding the cell performance.

Introduction

Solid oxide fuel cells (SOFCs) were investigated for several decades by many research institutions and companies (1,2). First approaches mainly used the electrolyte-supported cell (ESC) concept, operating at high temperatures up to 1000°C (1-4). In order to decrease the operation temperature, electrode-supported designs were developed. Cathode and anode-supported cells (CSCs or ASCs respectively) allow the implementation of a much thinner electrolyte layer, therefore reducing the ohmic losses considerably. Hence, these cells can be operated at intermediate temperatures, typically in the range of 650-850°C. This moderate temperature allows for the use of cheap ferritic steel as interconnector material as well as lowers the thermal exposure of other components (4). Recently, metal-supported SOFCs (MSCs), implementing a porous metal as the mechanical supporting structure of the cell, are considered especially attractive for the use in mobile applications such as auxiliary power units (APUs) or

range extenders in battery electric vehicles (BEVs). This is due to the improved robustness against thermal and redox cycles as well as vibrations (5-13). In tight cooperation with Forschungszentrum Jülich GmbH (“JÜLICH”, Germany), Plansee SE (“PSE”, Austria) developed an MSC concept based on their ITM[®] substrate, which supports the functional layers.(14-17) MSC stacks are under development by PSE in another project. AVL List (Austria) as engineering service provider is testing the produced cells in stacks and systems for commercial use (6,18).

State-of-the-art planar MSCs, manufactured by PSE consist of the porous ITM substrate, a Ni/8YSZ dual-phase cermet graded anode (8YSZ – with 8 mol-% yttria stabilized zirconia), a magnetron sputtered 8YSZ solid oxide electrolyte a Ce_{0.8}Gd_{0.2}O_{2-δ} (Gadolinium doped Ceria – GDC) diffusion barrier layer, and the A-site deficient perovskite type cathode La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) (15,16,18). A considerable difference in the fabrication of MSCs, in comparison to the well-known ASC production, is the absence of a separate cathode sintering process. This is due to the contradicting requirements of the metallic substrate and the cathode material in terms of thermal treatment. Whereas ITM and Ni in the anode are usually sintered under reducing conditions in order to prevent oxidation, the LSCF perovskite phase requires high oxygen contents to ensure the phase stability. As a compromise, current MSC cathode layers are assembled in the green state (15,18-22). Burn out of the organics (at 350-400°C) and sintering of the cathode is performed during onset of the cell operation. The in-situ activation temperature of 850°C is low in comparison to the temperature of 1040 °C used for ASC sintering (23), resulting in weaker bonding of the cathode to the DBL. The present study is targeting the issue of reduced cathode adherence on the DBL. Introduction of an ex-situ sintering procedure under controlled atmosphere with low p(O₂) and careful investigation of the phase stability properties of LSCF, based on a previous work (24), is aiming on improving the adherence and reliability of the cathode layer. As a result of increased mechanical stability of the cathode/electrolyte compound structure, cathode related degradation of MSCs is considered to decrease significantly.

Experimental

Based on the previous research (24), ex-situ sintering of complete MSC cells with LSCF cathode – performed at 950°C under Ar(5.0) (meaning 99.999 % purity argon) atmosphere – was scaled up from small samples with dimensions of 15x15 mm² to single cells with a size of 50x50 mm² enabling electrochemical characterization. Whereas the pure Ar(5.0) atmosphere, according to the specifications, provides a p(O₂) < 2 · 10⁻⁶ bar, the apparent oxygen partial pressure during the sintering process further decreases due to oxidation of the ITM substrate. Therefore, a precise control of the oxygen content of the atmosphere is difficult to achieve, since it not only depends on the gas supply but is also affected by the amount of porous metal, i.e. the number or size of cells sintered within one run. Consequently, the mechanical stability of the cathode layer was affected by the scale up as well. This needed to be considered when investigating the phase stability and phase transformation respectively. The phase composition of the prepared cells was analyzed via XRD (Empyrean, PANalytical GmbH, Germany or D4 Endeavor, Bruker Corp., USA) after ex-situ sintering and after the cell operation. Single cell measurements were conducted at JÜLICH (IEK-9) on cells with 16 cm² active cathode area. 533 ml/min H₂/3%H₂O and 666 ml/min air were supplied as fuel and oxidant respectively.

I/V-curves were measured from OCV to about 0.65 V in the temperature range from 850 to 650°C in steps of 50°C. Microstructural analysis was performed on polished cross-sections of tested cells, using SEM images (TM3000, Hitachi, Japan).

Results and Discussion

Two 50 x 50 mm² cells with 40 x 40 mm² LSCF cathode were sintered under Ar(5.0) atmosphere at 950°C for 3 h for subsequent electrochemical characterization. After sintering, the cells were stored for one week in ambient air, before the scheduled measurement of the electrochemical properties. Partial detachment of the sintered cathodes was observed. This kind of failure was attributed primarily to the scale-up to larger cells, while it was not obtained on model samples in the previous experiments. For further investigation of the cause of failure, cells with different geometry and various cathode dimensions were prepared and sintered. The largest cells with a size of 50 x 50 mm² were manufactured with plane 40 x 40 mm² cathodes or with cathodes segmented into 16 smaller areas of 9.25 x 9.25 mm². Further cell geometries used were 20 x 20 mm² cathodes on 25 x 25 mm² substrates, and a Ø 10 mm cathode on a 15 mm button-cell. All cells were sintered in one run. Failure of the cathode layers was obtained within one day of storage in ambient air, independent of the cell/layer dimensions. Hence, it was concluded, that the reducing conditions of the atmosphere during sintering mainly affect the layer stability, whereas the influence of the cathode dimension is less pronounced. Figure 1 shows the XRD pattern of the 20 x 20 mm² cathode immediately after sintering. The obtained phase composition revealed a pronounced phase decomposition of the LSCF perovskite, resulting in a tetragonal AB₂O₄ phase, La₂O₃, and CoFe.

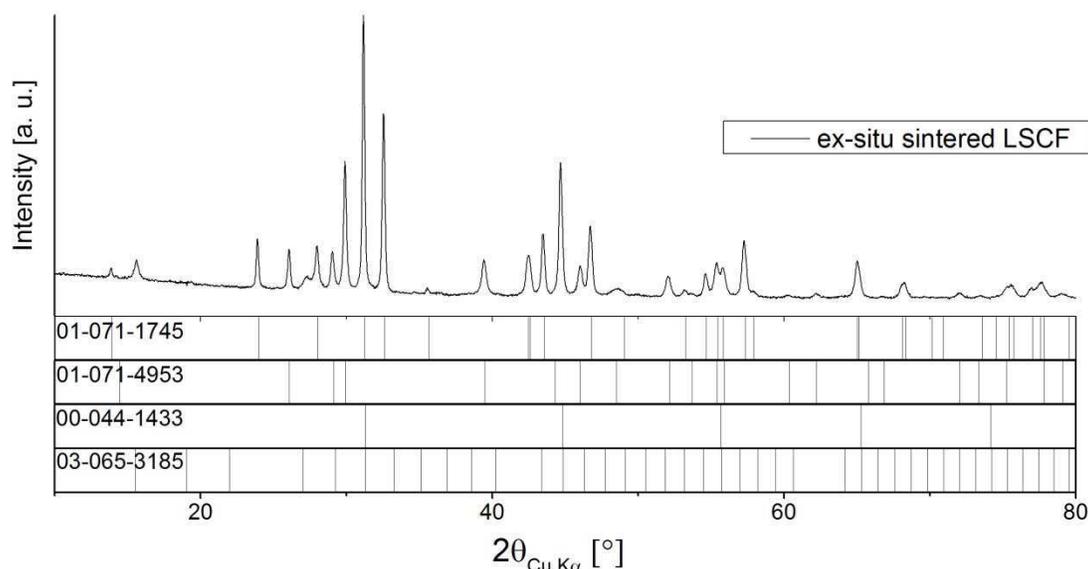


Figure 1. XRD analysis of a 20 x 20 mm² LSCF cathode sintered under Ar(5.0) at 950°C for 3 h. Measurement conducted immediately after sintering.

From this result it was concluded that the formation of La₂O₃ is the most critical point regarding the stability of the cathode layer. La₂O₃ is known to be strongly hygroscopic. On exposure to ambient air, it reacts with the atmospheric humidity, forming La(OH)₃.

(25). This reaction is accompanied with a volume increase of $> 70 \%$, therefore leading to failure of functional layers in which it is incorporated (26). The higher the amount of La_2O_3 formed during sintering, the higher is the susceptibility of the resulting layer to humidity from air, associated with subsequent mechanical failure. This is in accordance with the behavior observed in this work. Layers containing higher La_2O_3 contents fail earlier than layers sintered under mild conditions with higher $p(\text{O}_2)$. As the formation of small amounts of La_2O_3 could not be avoided reliably in our experiments, the produced cells either need to be operated immediately, or have to be effectively protected from humidity. By considering these requirements, electrochemical characterization of cells with ex-situ sintered cathode was performed successfully. Moreover, XRD analysis of a tested cell confirmed the reversible phase transformation taking place during the first hours of cell operation, as shown in Figure 2.

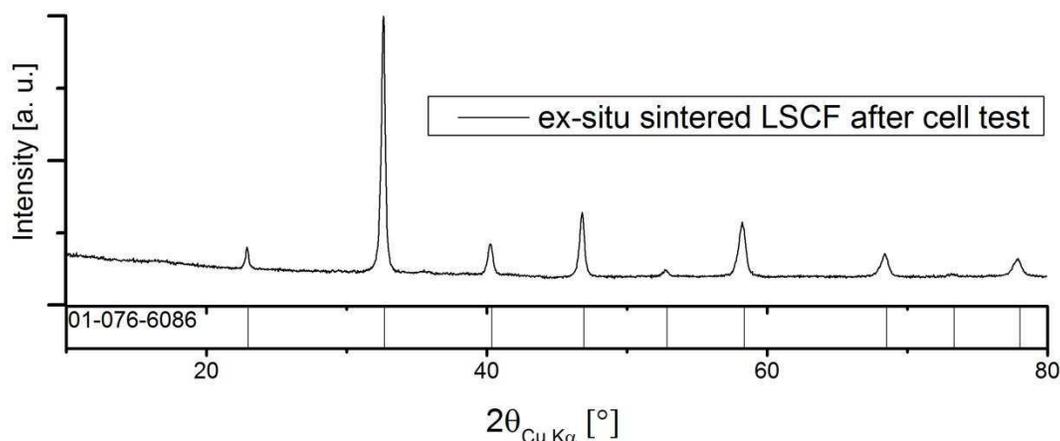


Figure 2. XRD analysis of the ex-situ sintered LSCF cathode layer after cell operation.

The obtained electrochemical performance of an ex-situ sintered MSC is shown in Figure 3. The measured OCV of 1.04-1.07 V at 850-650°C, as well as the fluctuation of the measured curves, indicates the occurrence of slight leakage within the setup. This leakage can either result from small electrolyte defects or from non-optimum sealing of the glass solder. Nonetheless, the sealing quality was still sufficient for recording the I/V-curves, enabling a comparison to state-of-the-art cells containing LSCF cathodes, which were in-situ activated at 850 °C. At the working point of 0.7 V, current densities of 1.30, 1.15, 0.96, 0.60 and 0.35 A/cm² at 850, 800, 750, 700 and 650°C were measured for the cell with ex-situ sintered LSCF cathode. This corresponds to a performance increase of 8-17 % in the temperature range of 700-850°C compared to state-of-the-art cells. After the test, the cathode still showed good adherence and mechanical stability. An SEM image of a polished cross section is shown in Figure 4. The microstructure of the ex-situ sintered LSCF cathode is finer compared to standard ASC cathodes fabricated in JÜLICH. This is due to the lower sintering temperature of 950°C compared to 1040°C applied for cathode sintering in the case of ASCs. No microstructural anomalies were observed for the other cell components. Hence, the ex-situ sintering procedure in Ar atmosphere was confirmed to be applicable to MSCs for fabricating cathodes with improved adherence and good electrochemical performance.

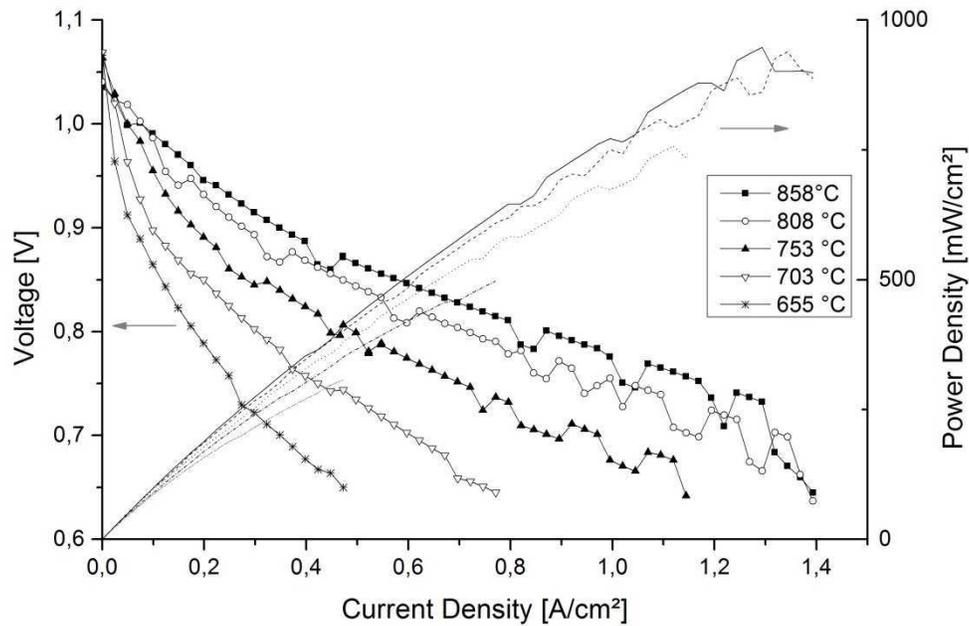


Figure 3. I/V-curves and resulting power density of an MSC with ex-situ sintered LSCF cathode.

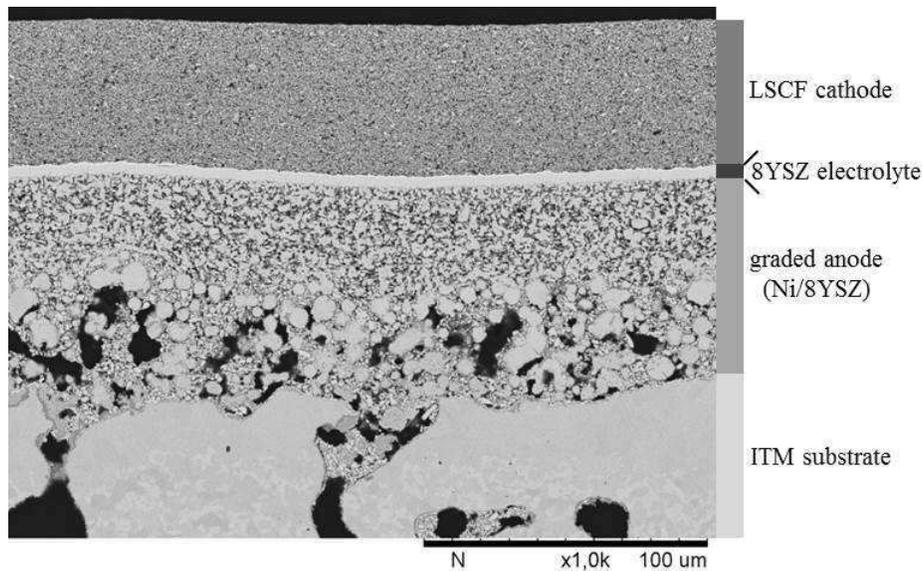


Figure 4. SEM image of a polished cross section of an MSC with ex-situ sintered cathode after electrochemical characterization.

Conclusions

Metal-supported solid oxide fuel cells offer high potential for implementing SOFCs in mobile applications such as auxiliary power units or range extenders for battery electric vehicles. This is due to the expected high mechanical robustness, especially required to withstand fast thermal cycles and vibrations. One of the issues in current MSC production is the insufficient adherence of the cathode layer. Due to contradicting

requirements for the porous metal support (ITM) and the LSCF cathode in terms of the optimum $p(\text{O}_2)$ of the sintering atmosphere, cathodes are usually applied in the green state and in-situ activated during the onset of operation. Here, the applied temperature usually is in the range of 850°C, which does not provide a good adherence of the cathode on the diffusion barrier layer. In the present work, an innovative ex-situ sintering procedure was developed, which can be applied to complete MSCs, without irreversibly damaging the oxygen-sensitive cell components like metal substrate or Ni in the anode. Sintering was performed in Ar(5.0) atmosphere at 950°C for 3 h, leading to a moderate phase decomposition of LSCF, which was found to be reversible upon heating in ambient air. Nevertheless, it must be ensured that the exposure of the ex-situ sintered cathode to atmospheric humidity is kept to a minimum. After sintering the cell was successfully operated. The obtained cell performance confirmed the electrochemical activity of the LSCF cathode after the reversible phase transformation. Furthermore, a performance increase of 8-17% in the range of 700-850°C in comparison to state-of-the-art cells with in-situ activated cathodes was observed. The XRD analysis after the single cell measurement confirmed the reversible phase transformation back to LSCF perovskite during the cell test. Microstructural analysis did not reveal damage of the other cell components. Therefore, the obtained results are very promising for achieving a substantial improvement of the cathode reliability and reaching high performance of MSCs at the same time.

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