Novel Processing of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ Cathodes for Metal-Supported Fuel Cells

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Highlights

- Novel processing of LSCF cathodes for metal-supported fuel cells
- Ex-situ sintering in Ar at 950 °C for 3 h
- Significantly improved mechanical adherence
- Reliable protection of the metallic substrate against oxidation
- Avoiding the decomposition of the LSCF cathode

Abstract

Metal-supported solid oxide fuel cells (MSCs) have gained high attention as they offer a possibility to utilize solid oxide fuel cells (SOFCs) in mobile applications such as auxiliary power units in heavy duty vehicles. Cathode reliability is one of the main issues of MSC development, since cathodes tend to degrade rapidly after being in-situ activated during onset of the stack operation. In the present study, a novel sintering route for $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode material was developed. Sintering of the screen printed cathodes was performed before stack operation at 950 °C in reducing Ar atmosphere for 3 h. Under these conditions, severe oxidation of the metallic substrate and the Ni in the anode was avoided reliably.

For proof of concept, phase stability and microstructure of the MSC cathodes were characterized. The results reveal that cathode layers sintered in Ar exhibit substantially improved adherence and mechanical stability compared to conventionally processed MSC cathodes, making them ready for systematic investigation of electrochemical performance.

Keywords

LSCF; SOFC; Phase Stability; Sintering Behavior; Metal-Supported Fuel Cell; Cathode Adherence

Introduction

Anode supported solid oxide fuel cells (ASCs) have been developed to an outstanding performance and durability level at Forschungszentrum Jülich GmbH [1]. However, the anode-supported design is particularly suitable for stationary applications due to the brittleness of the ceramic material and its vulnerability in terms of fast thermal cycling. Therefore the MSC concept is thought to extend the field of use to non-stationary applications. Various groups and research institutions have been working on the implementation of MSCs during the past years in order to take advantage of their promising characteristics.[2-6] The MSC design of Plansee SE (Reutte, Austria) was developed in close cooperation with JÜLICH since 2008.[7] Compared to ceramics, the metallic support is more robust in terms of stresses arising from vibrations or thermal cycles.[8, 9] Nonetheless, there are restrictions limiting current MSC performance and long-term stability. One of these issues concerns the processing of the cathode layer. The fabrication of cathodes for MSCs cannot be conducted in the same way as for ASCs. This is due to the strong oxidation of the metal substrate and the nickel of the anode occurring if sintering is performed in ambient air. Reducing sintering conditions such as hydrogen atmosphere are preferred for MSCs to avoid detrimental oxidation effects. Though, cathode materials like LSCF decompose during thermal treatment in strongly reducing atmosphere. As a compromise, current MSC cathodes are utilized for stacking in the green state and in-situ activated during stack assembling and startup at 850 °C for 100 h. These in-situ activated cathodes show poor adherence to the $Ce_{1-x}Gd_xO_{2-\delta}$ (GDC – gadolinium doped ceria) diffusion barrier layer (DBL) and limited mechanical stability leading to degradation during long-term operation of cells.[7, 8, 10, 11]

In the present study, a novel sintering route of LSCF cathodes was developed, which focuses on sintering of the cathodes under controlled reducing conditions before stack operation. First investigations were conducted on pure cathode material, which was pressed into pellets and sintered in atmospheres with varying oxygen partial pressure (p_{O2}) to study the related shrinkage and phase stability. As reference, sintering in ambient air was performed. Next, the preferred sintering conditions were applied to screen printed cathode layers to take into account mechanical stability and durability of the sintered layers. Finally, the acquired knowledge was transferred to cathode layers screen printed on MSC half cells to proof the layer adherence and mechanical stability resulting from the applied conditions.

Experimental

The LSCF cathode powder was synthesized in-house by spray drying, subsequent calcination at 900 °C, wet milling to an average particle size of $d_{50} = 0.8 \pm 0.1$ µm and drying at 70 °C.

Investigation of the phase stability and the sintering behavior were carried out using uniaxially cold pressed samples (100 MPa, 120 s, 8 mm diameter). The sintering behavior was analyzed in various atmospheres using a Netsch DIL 402C dilatometer. The atmospheres for initial experiments were Air, Ar(5.0) and dry Ar/2.9%H_2, representing standard ambient air atmosphere ($p_{O2} = 10^3$ Pa), slightly reducing ($p_{O2} \approx 1$ Pa) and significantly reducing ($p_{O2} \approx 10^{-15}$ Pa) atmosphere. Sintering temperature was varied between 800 and 1100 °C. Further investigation was conducted by including the ITM substrate material (Plansee SE) to the sintering process of LSCF pellets in argon atmosphere in order to examine the influence of the metallic substrate on the phase stability of LSCF during sintering. After dilatometry the phase composition of the sintered samples was analyzed via XRD (D4 Endeavor, Bruker Corp., USA) to estimate applicable p_{O2} for cathode sintering. The acquired sintering conditions were transferred to sintering of LSCF layers screen printed on 8YSZ substrates (200 µm thickness, Kerafol, Germany) or MSC half cells (Plansee SE) respectively. A GDC diffusion barrier layer was coated on 8YSZ substrates as well as on electrolyte layers by magnetron sputtering. The influence of different sintering temperatures and atmospheres on the adherence and mechanical stability of cathode layers was estimated by investigating screen printed LSCF on GDC coated 8YSZ substrates. In the case of on-setting phase decomposition, controlled reoxidation of the LSCF layers by annealing at 800 °C in ambient air (stack operation conditions) was investigated. Microstructure of the MSC cathodes was analyzed by SEM (Ultra 55, Zeiss, Germany).

Results

XRD analysis of samples sintered in the dilatometry study disqualified Ar/2.9%H_2 atmosphere as severe decomposition of the cathode material occurred. Since strong phase decomposition during fabrication is detrimental for the application as cathode material, sintering in Ar/2.9%H_2 was not considered in further experiments. In contrast, diffraction patterns of LSCF pellets sintered in Ar at temperatures up to 1100 °C did not reveal any phase decomposition (XRD spectra obtained from pellets not shown here). Dilatometry indicated an enhanced sintering activity when thermal treatment was conducted in Ar, compared to the sintering in ambient air, as shown in Fig. 1. Obviously, this increase of the sintering activity becomes more pronounced with increasing sintering temperature. This is likely due to the increasing formation of oxygen vacancies in low p_{O2} environments, which is coupled with a higher mobility of cations due to valence change. A related study was conducted recently on GDC by Esposito et al. [12] which also includes an explanation for increased sintering activity of MIEC ceramics at low p_{O2}.

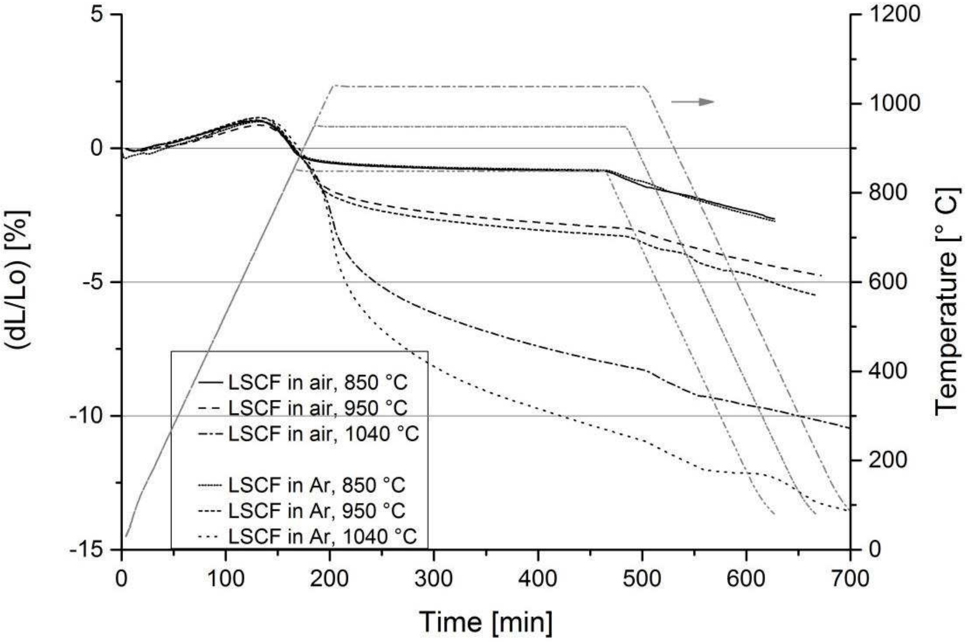


Fig.1:

This enhanced sintering is thought to improve mechanical stability of the cathode layer and adherence to the DBL due to intensified interaction between the layers and higher densification. Accordingly, Ar atmosphere was chosen for further experiments in order to take advantage of improved sintering of LSCF and to prevent strong oxidation of ITM substrate and anode.

The presence of porous ITM substrate material during the sintering of LSCF pellets in Ar revealed a remarkable p_{O2} decrease by gettering residual oxygen from the Ar, hence influencing the phase stability of LSCF. XRD patterns of pellets sintered in Ar in presence of ITM exhibit reflexes corresponding to K_2NiF_4 type structure and identified as tetragonal (I4/mmm) $LaSrFeO_4$, as well as cubic Fe and $SrCoO_{2.29}$ structures. Sintering of the screen-printed LSCF layers gave information about layer stability resulting from various sintering conditions. In an adhesive tape (pull-off) test, it was clearly observed that a sintering temperature of

950-1040 °C results in a considerably stronger adherence of the LSCF cathode layer compared to layers sintered at 850 or 900 °C. This indicates that a sintering temperature higher than 900 °C should be chosen to improve the reliability of MSC cathodes. Sintering in Ar caused slight phase decomposition contrary to the observed phase stability of pellets. Fig. 2 shows the XRD patterns of LSCF layers screen printed on electrolyte substrates and an MSC half-cell respectively. The diffractogram of an LSCF layer on 8YSZ/GDC sintered in Ar at 950 °C (Fig. 2b) shows reflexes corresponding to the structures of $LaSrFeO_4$, Co and Fe in addition to reflexes of the initially present perovskite structure (Fig. 2d). This difference of phase stability in comparison to the results achieved on pressed pellets is thought to originate from the high specific surface area of the screen-printed layer. Hence, the apparent reducing Ar atmosphere can penetrate the layer easily and cause notable phase transformation of the material.

The layers sintered in Ar were reoxidized at 800 °C for 3 h in ambient air in order to investigate the reversibility of the phase decomposition. A phase transformation back to perovskite $(La,Sr)(Co,Fe)O_{3-\delta}$ structures was observed (Fig. 2c). The phase fractions were calculated to 51 % LSCF in rhombohedral structure, 48 % cubic LSCF, and < 1 % Co_3O_4 by Rietveld refinement. Moreover, the reoxidized layers did not show any mechanical failure. Transfer of the selected sintering procedure to sintering of MSC cathode layers was performed. Sintering of screen printed LSCF cathodes of 10 x 10 mm² on 15 x 15 mm² MSC samples for 3 h in Ar at 850, 950 and 1040 °C respectively gave further information to select optimum sintering conditions applicable for MSC cathodes. XRD analysis subsequent to the cathode sintering confirmed the occurrence of phase transformation. Amounts of $LaSrFeO_4$ and Co/Fe increased with the sintering temperature. Small amounts of La_2O_3 (1 % after sintering at 950 °C, 7 % at 1040 °C) were detected as well (Fig. 2a).

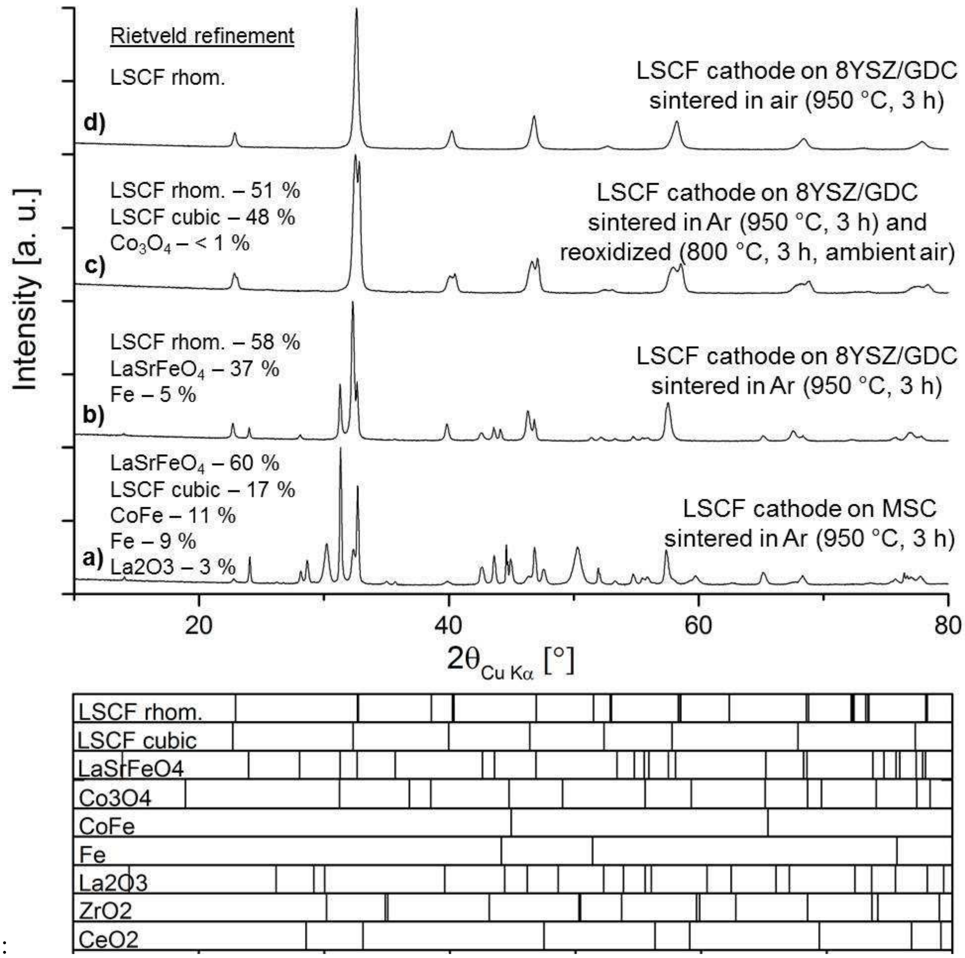
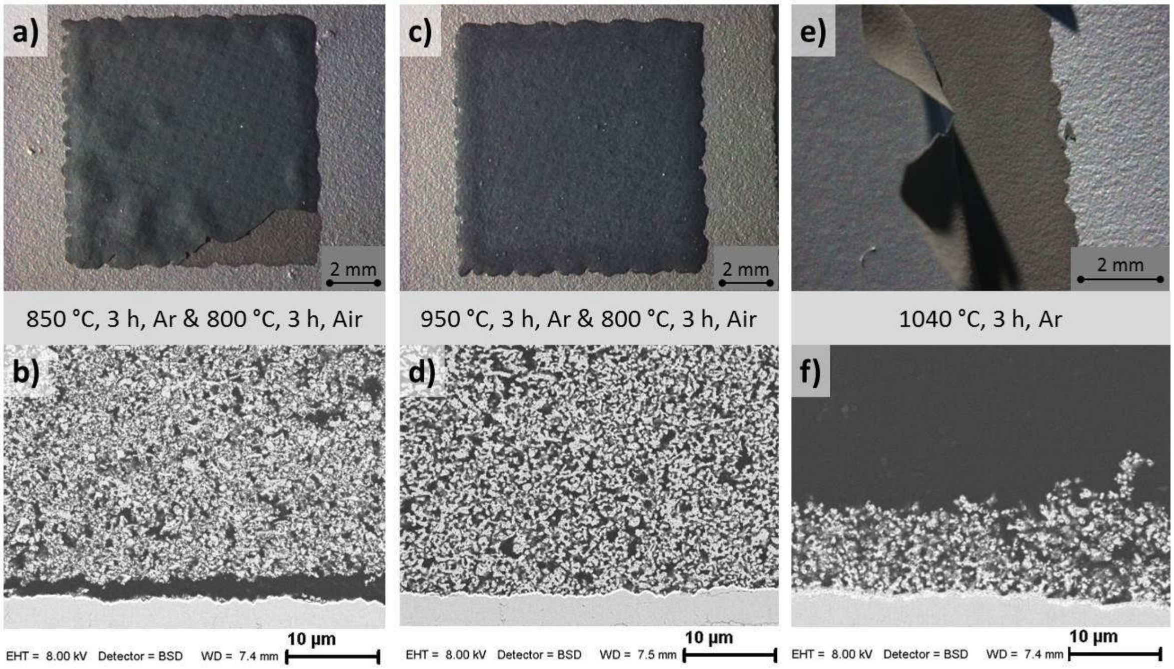


Fig. 2:

After sintering, the LSCF was reoxidized for 3 h at 800°C in ambient air. Fig. 3 shows the appearance of the cathode layer after reoxidation depending on the different sintering conditions. After sintering at 850 °C in Ar the cathode adhered on the surface of the MSC half-cell (not shown). This observation indicates that previous sintering at 850 °C in Ar did not cause high stresses due to the in-plane geometrical constraint or phase transformation which would damage the layer. Nevertheless, subsequent reoxidation at 800 °C in air resulted in failure of the cathode layer, which occurred at the interface between the cathode and the DBL (Fig. 3a/b). In sum, the low sintering temperature of 850 °C did not provide sufficient bonding of the cathode layer to the DBL, leading to delamination due to stresses obviously occurring during reoxidation.

Fig. 3:



The cathode layer sintered in Ar at 950 °C and subsequently reoxidized at 800 °C in ambient air did not reveal any mechanical failure (Fig. 3c/d). Furthermore, the microstructure matched closely to the microstructure of LSCF cathodes sintered under JÜLICH ASC conditions at 1040 °C, 3 h in air. In contrast, the cathode layer sintered on the MSC half-cell at 1040 °C in Ar showed partial delamination already after sintering (Fig. 3e/f). SEM analysis revealed failure within the cathode layer, close to the cathode/DBL interface. It is expected that the enhanced sintering of LSCF in reducing atmosphere and the clearly pronounced phase transformation induce high stresses in the cathode layer due to increased layer strain misfit, causing the failure already during sintering. By comparison of the obtained results it is supposed that sintering at a temperature of 950 °C led to the best compromise regarding sufficient layer adherence and reversibility of the phase transformation. These conditions are the basis for systematic electrochemical studies on sintered MSCs.

Conclusions and Outlook

Sintering of LSCF in argon atmosphere was found to lead to moderate and reversible phase transformation. During sintering the initial perovskite structure was partly transformed to a tetragonal $LaSrFeO_4$ structure which was reversibly transformed back to $(LaSr)(CoFe)O_{3-\delta}$ perovskite structures upon reoxidation in ambient air at 800 °C. Presence of the ITM substrate material lowers the effective oxygen partial pressure during the sintering process, giving rise to partial phase transformation, without leading to unacceptable strong decomposition of the material. Poor adherence to the DBL was obtained when sintering was performed at temperatures as low as 850-900 °C. Remarkably stronger adherence resulted from sintering at 950-1040 °C. For MSC full cells an intermediate temperature of 950 °C prevented layer failure by avoiding strong phase decomposition and high sintering stresses. Furthermore, it ensures sufficient bonding of the cathode to the DBL, preventing early failure due to delamination. Therefore, ex-situ sintering in Ar atmosphere at a temperature of 950 °C is a promising concept to increase reliability of MSC cathodes.

In near future, electrochemical performance of cathodes processed by the novel sintering route will be investigated. Long-term stability of sintered MSC cathode layers has to be proven as well.

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Figure Captions

1. Comparison of linear shrinkage of LSCF pellets by dilatometry in ambient air and Argon at 850 °C, 950 °C and 1040 °C respectively.
2. XRD patterns of screen printed LSCF cathode layers sintered in various atmospheres. a) LSCF cathode on MSC half-cell sintered in Ar at 950 °C for 3 h; b) LSCF cathode on 8YSZ/GDC electrolyte substrate sintered in Ar at 950 °C for 3 h; c) sample (b) reoxidized at 800 °C for 3 h in ambient air; d) LSCF on 8YSZ/GDC sintered in ambient air at 950 °C for 3 h. (CeO_2 not included to Rietveld refinement; ZrO_2 excluded after refinement as corresponding reflexes originate from the substrate) Powder Diffraction Files: LSCF cubic – 00-946-0335; $LaSrFeO_4$ – 01-071-1745; Co_3O_4 –

01-080-1533; CoFe – 00-049-1568; Fe – 96-901-5446; La_2O_3 – 01-074-1144; ZrO_2 – 01-070-4429; CeO_2 – 00-004-0593; for Rietveld refinement used files representing rhombohedral LSCF – 00-049-0285, 01-082-1963, 01-086-1665.

3. Illustration of MSC cathode layer adherence depending on the sintering temperature in Argon. a-b) sintered at 850 °C for 3 h in Ar & subsequent reoxidation at 800 °C for 3 h in air; c-d) 950 °C, 3 h in Ar & reoxidized; e-f) sintered at 1040 °C for 3 h in Ar. (Top images – stereo microscope, bottom images – SEM)

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