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Ex Situ Sintering of Dual-Phase Cathodes for Metal-Supported Fuel Cells

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Abstract

One of the main challenges in manufacturing of metal-supported fuel cells (MSCs) is the cathode processing. Established cathode sintering in ambient air leads to strong oxidation of the metal substrate and the Ni phase in the anode. Therefore, MSC cathodes are often activated in situ immediately after sealing of the gas compartments, by feeding air on the cathode side. Unfortunately, in situ activation leads to restrictions regarding cathode adherence. Recently, an ex situ sintering approach was developed for LSCF cathodes based on sintering the cathode in Argon before cell operation, clearly improving cathode adherence. Not unexpected, sintering in Argon leads to partial decomposition of LSCF. However, this decomposition was found to be reversible upon heating with air flow during first hours of cell operation. Ex situ sintering leads to a clearly improved cathode adherence. Nonetheless, careful protection from air humidity has to be ensured during storage of ex situ sintered cells, since some decomposition products are sensitive to hydroxide formation coupled with cathode exfoliation due to volume expansion. In the present work, the ex situ sintering approach was adapted to dual phase cathodes consisting of LSCF/GDC and LSC/GDC for the first time. In this case, no failure of the ex situ sintered layers was observed during storage in ambient air. Again, phase decomposition occurred due to low oxygen partial pressure, which was superposed by reactions between perovskite and GDC. Therefore, reversibility of the decomposition was investigated by XRD analysis on model samples. First promising electrochemical results reveal the potential of this new sintering approach, which is of special interest for industrial application of MSCs.

Introduction

Solid oxide fuel cells (SOFC) are electrochemical energy converters, which directly convert chemical energy stored in fuels into electrical energy. This direct conversion enables an increased efficiency compared to established combustion-based power generators, as there are no intermediate conversion steps which reduce the overall efficiency. A further advantage of fuel cell generators is their silent operation, as the cells do not include moving parts. Due to the fuel flexibility of SOFCs, these cells can be operated with a wide range of fossil fuels like natural gas or Diesel as well as fuels made from renewable energy like hydrogen or (bio-)ethanol. Hence, SOFCs present a promising technology to contribute to both, the transition period to clean power generation as well as future energy supply based on renewables including technologies like wind and solar. [1-4]

Metal-supported SOFCs (MSC) are developed in order to extend the field of use of SOFCs to mobile applications like auxiliary power units for heavy-duty vehicles or range extenders for battery electric vehicles. MSCs are fabricated based on a porous metal support, which exhibits the required properties like increased ruggedness against vibration, thermal cycles, or improved redox behavior. For this approach, different MSC concepts were developed by various institutions. [5-12] The MSC concept of Plansee SE (Austria) has been developed in close cooperation with Forschungszentrum Jülich GmbH (Germany) since 2008. [13-18] In this work, processing of MSC cathodes was further improved, aiming at sufficient adherence after ex situ sintering, tolerance against humidity of cells sintered ex situ, and high electrochemical performance of the cathode. Specific sintering conditions to protect the metallic substrate from oxidation were taken into account carefully.

1. Scientific Approach

Cathode sintering under ambient air conditions cannot be applied to MSCs due to strong oxidation of the metal substrate during a thermal treatment in oxidizing atmosphere. Therefore MSC cathodes are usually fabricated by either an infiltration process which does not require a high-temperature sintering step or an in situ activation of the cathode layer during the first hours of cell operation [6, 12, 19]. Operation of infiltrated cathodes often suffers from coarsening of the very fine particles of the catalyst, leading to fast degradation due to loss of active sites. Cathodes activated in situ frequently exhibit poor adhesion due to the comparably low activation temperature, giving rise to degradation by partial delamination at the cathode-electrolyte interface and loss of active cell area. Recently, a novel ex situ sintering approach has been developed for LSCF cathodes on Plansee MSCs [13, 20, 21]. Sintering of complete cells under a controlled argon atmosphere clearly improved the adherence of the fabricated cathode layer. Proof of concept was successfully completed by operating cells with cathodes sintered ex situ. A slight increase in cell performance compared to standard cells activated in situ was obtained [20]. Nonetheless, issues regarding the reliability of these cathodes are still remaining. This mainly includes susceptibility to spallation of the sintered cathode layer during storage under ambient conditions. Partial decomposition of LSCF during ex situ sintering leads to formation of La_2O_3 . Even small amounts of this phase may cause failure of the layer due to volume expansion when reacting with humidity from ambient air to $\text{La}(\text{OH})_3$. This can be postponed by encapsulating the sintered cell in airtight foil pouches [20]. However, this approach is not suitable for long-term storage in an industrial environment. Moreover, it complicates the handling of the cells. Therefore, further improvement of the fabrication procedure is necessary for industrial application. As the next step of development, the use of dual-phase cathodes of perovskite material mixed with GDC is presented in this paper.

It is expected that addition of this second phase increases stability and reliability of the cathode due to i) the formation of a mechanically supporting GDC network, preventing exfoliation of the decomposed perovskite, and ii) reduction of the thermal expansion of the (dual-phase) cathode layer, thereby lowering the stress level in the sintered layer.

2. Experiments

MSC half cells were provided by Plansee SE. The cells are fabricated based on the porous ITM (Intermediate Temperature Metal) substrate of Plansee produced by powder metallurgy [22, 23]. Subsequently, the layered cell structure is applied on this substrate. First, a GDC barrier layer is deposited by magnetron sputtering in order to prevent interdiffusion of elements from substrate (Fe, Cr) and anode (Ni). The graded Ni/YSZ anode is applied by screen printing three layers with decreasing particle size, in order to cover the large pores of the substrate and provide a smooth surface for application of the dense electrolyte. Each layer is sintered under a hydrogen atmosphere to prevent oxidation of the metal. The YSZ electrolyte is applied by gas flow sputtering. Another GDC barrier layer is applied by magnetron sputtering to prevent reaction between electrolyte and cathode. The final step of cell fabrication is screen printing of the cathode (LSCF, LSC or mixtures thereof with GDC). Detailed information about the cell processing can be found elsewhere [24-27].

Cells sized 50 x 50 mm² with 40 x 40 mm² active cathode area were fabricated and used for single-cell measurements. Model samples sized 25 x 25 mm² with 20 x 20 mm² cathode were used for preliminary investigation of the layer stability. For ex situ sintering, complete cells were thermally treated in a tube furnace (80 mm diameter alumina tube, 750 mm heated length, Nabertherm, Germany) equipped with an oxygen sensor to monitor the oxygen partial pressure during sintering of the cathode. Ar(5.0), i.e. 99.999 % pure Ar, was supplied at a flow rate of 840 sccm. Ex situ sintering was conducted at 950 °C for 3 h. Single cell measurements were performed using a commercially available test rig from EBZ GmbH (Dresden, Germany) equipped with an in-house developed all ceramic sample holder. Cells were sealed for 10 h at 850 °C between two thin YSZ frames using a glass sealant developed at ZEA-1 (Forschungszentrum Jülich GmbH) [28]. Dry hydrogen was supplied as fuel at a flow rate of 1000 sccm, and air (2000 sccm) as oxidant. Current-Voltage curves were measured between 850 and 650 °C in steps of 50 K.

After operation the cells were analyzed by XRD and SEM in order to determine the phase composition and microstructure.

3. Results

In previous experiments, it was found that MSCs with LSCF cathode sintered ex situ perform slightly better compared to state-of-the-art cells, which were activated in situ during cell operation [20]. As new test benches and increased gas flow rates were used for the present measurements, cells with pure LSCF perovskite cathodes sintered ex situ were tested as a reference first. Two cells of this type were tested. The first cell was sintered ex situ immediately before testing in order to limit exposure to humidity from air. The other cell was already sintered ex situ in the context of our work published recently [20] and was stored afterward for one year encapsulated in a foil pouch. When the foil pouch was opened before the measurement, a distinct color change was visible, but no spallation of the cathode layer was observed. Fig. 1 shows the IV curves measured between 850 and 700 °C operating temperature. A moderate performance of 0.6 A/cm² at a cell voltage of 0.7 V was obtained at 750 °C. After the test, buckling and partial

delamination of the cathode was observed, which might explain the limited performance. In contrary, the cell prepared immediately before testing showed superior performance as shown in Fig. 2. Measured current density of 1.32 A/cm² at 0.7 V and 750 °C is in good agreement with the performance of cells tested at Plansee almost reaching the value of 1.37 A/cm² previously achieved with LSC cathode [20]. In this case, good adherence of the cathode was observed after the test. The significantly increased performance compared to that of nominally identical cells published earlier [20] is due to the increased flow rate of the supplied fuel and air. An improved sealing procedure in the new test rig might contribute to a minor extent as well.

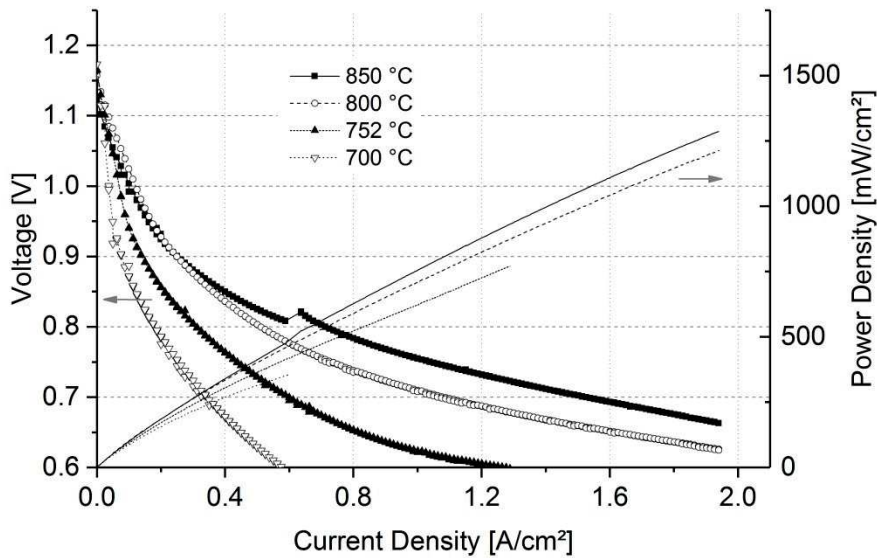


Fig. 1: IV characteristics of an MSC with LSCF cathode sintered ex situ, which was stored for 1 year encapsulated in a foil pouch.

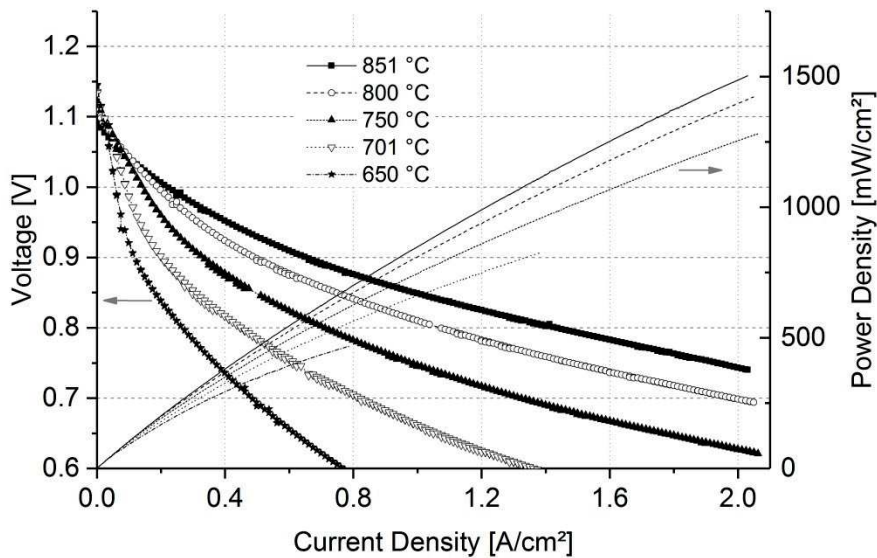


Fig. 2: IV characteristics of an MSC with LSCF cathode sintered ex situ, which was prepared shortly before the current experiments.

In preliminary experiments, the phase composition and layer stability of dual-phase cathodes LSCF/GDC and LSC/GDC, each in a 60/40 ratio, was investigated. 20 x 20 mm² cathode layers were printed on model samples of MSC half-cells or YSZ electrolyte substrates equipped with a GDC barrier layer and sintered at 950 °C under Ar or Ar/2.9%H₂ atmosphere. For both cathode compositions and regardless of the substrate

used, the dual-phase cathode layers revealed a clearly improved stability compared to pure perovskite cathodes. In contrast to pure LSCF cathodes, which fail within several days if stored under ambient conditions, dual-phase cathodes did not show delamination within 8 months under ambient air.

XRD analysis revealed a pronounced phase decomposition of the dual-phase cathodes after ex situ sintering, including a reaction product of Sr_2CeO_4 from interaction between perovskite and GDC. Nonetheless, the phase decomposition was observed to be reversible during cell operation, leading to – within the accuracy of XRD – full re-oxidation to GDC and perovskite.

Single cell measurements of cells with LSCF/GDC and LSC/GDC cathodes sintered ex situ were conducted under the same conditions as described for the cells with pure LSCF cathode. The results are shown in Fig. 3 (LSCF/GDC) and Fig. 4 (LSC/GDC). Whereas the LSCF/GDC cathode showed poor performance of about 0.5 A/cm^2 at 0.7 V and $750 \text{ }^\circ\text{C}$, the cell with LSC/GDC cathode performed well with a current density of 1.30 A/cm^2 . This is a promising result, as the microstructure of the dual-phase cathode is not optimized so far. For these preliminary experiments, the fabrication was based on using currently available powders of LSC and GDC. Optimization of the microstructure by adjustment of the particle size, perovskite/GDC ratio or sintering conditions is expected to result in further increase of performance.

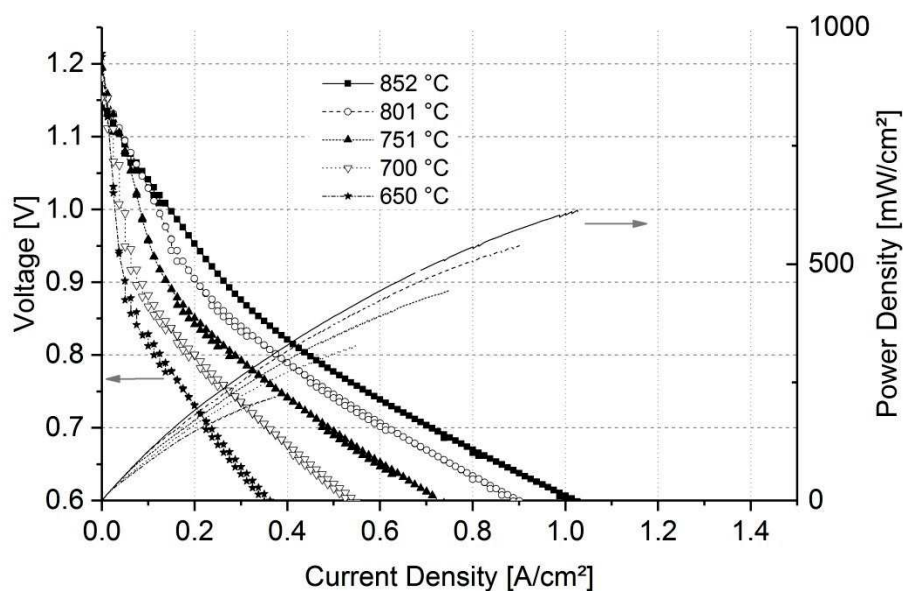


Fig. 3: IV characteristics of an MSC with LSCF/GDC cathode sintered ex situ.

SEM analysis of the tested cells revealed a slightly finer and denser microstructure of the dual-phase cathodes compared to the LSCF single-phase cathode, as shown in Fig. 5. Perovskite as well as GDC particles appeared to be homogeneously distributed in the cathode layer.

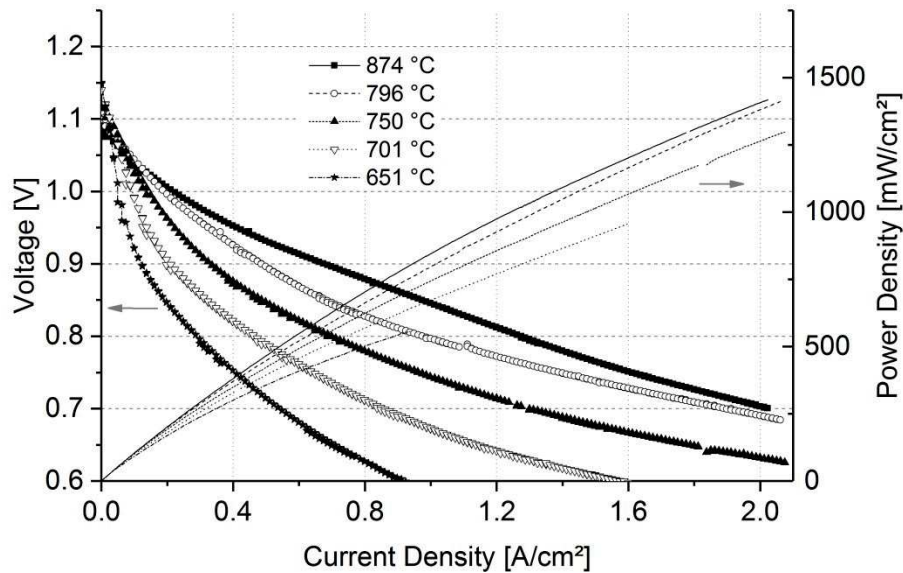


Fig. 4: IV characteristics of an MSC with LSC/GDC cathode sintered ex situ.

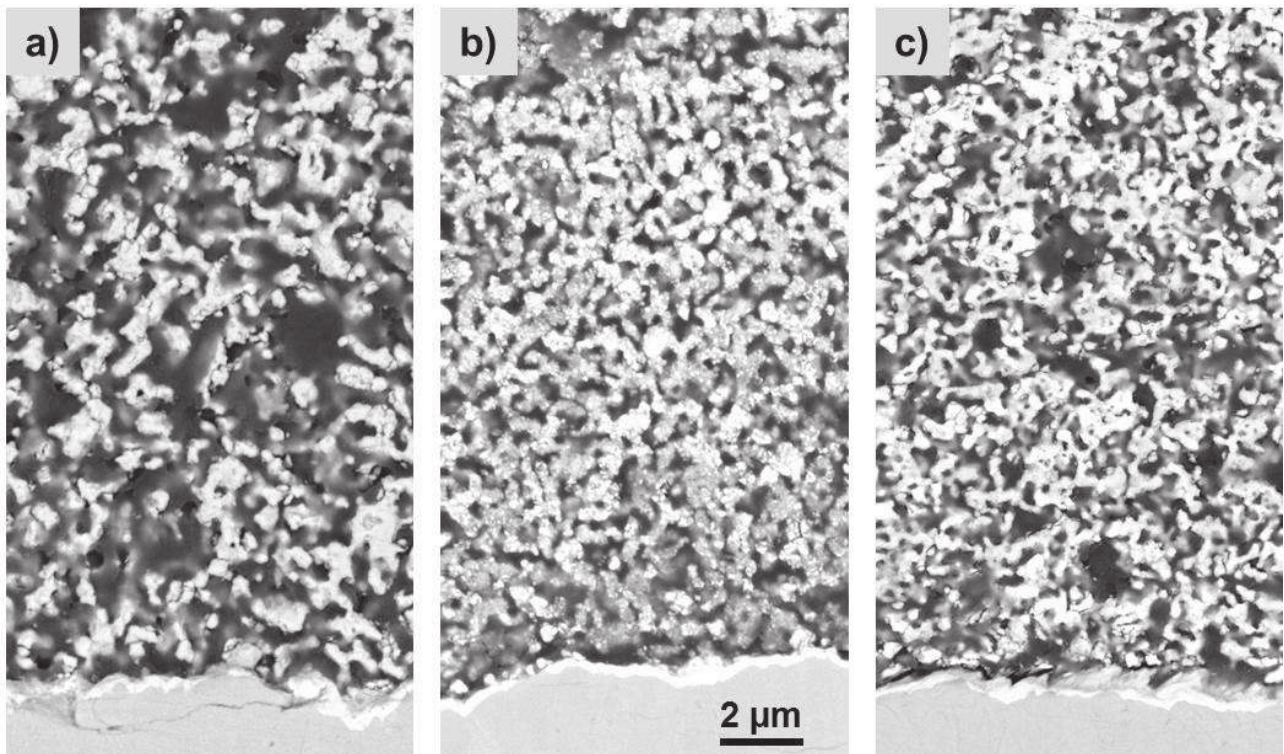


Fig. 5: SEM images of the cathodes after cell operation – a) LSCF, b) LSC/GDC, c) LSCF/GDC.

The beneficial effect of GDC addition to the active perovskite material, leading to improved stability of the cathodes, is expected to originate from the formation of a rigid network of GDC particles, interrupting the perovskite network and thereby preventing failure due to crack propagation. As La_2O_3 is still identified as a decomposition product in dual-phase cathodes sintered ex situ, GDC apparently does not significantly affect the decomposition of the perovskite. Also, the effect of lower coefficient of thermal expansion of the dual-phase material is expected to play a minor role in improving the reliability during storage. Nevertheless, lower thermal stress might be advantageous in terms of long-term performance.

4. Conclusions

As a conclusion, introduction of LSC/GDC dual-phase cathodes for MSCs significantly increases the layer stability and reliability during storage under ambient conditions. Hence, handling of the cells is facilitated, which is an important progress from an industrial point of view. Promising electrochemical performance was achieved despite non-optimized microstructure enabling further improvement, which will be part of our future work. Further experimental planning will also include long-term testing of cells with various cathode types, as well as application of the dual-phase cathode on cells with high-performance Ni/GDC anode.

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