THERMOCYCLIC LOAD: DELAMINATION DEFECTS AND ELECTRICAL PERFORMANCE OF SINGLE CELLS

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ABSTRACT

Single cells were thermal cycled and electrical measurements (I-V characteristics, impedance spectroscopy) were performed at operation conditions (950°C, anode: H₂ 0.5 l/min, cathode: air 0.5 l/min, electrode area: 10 cm²). The degradation caused by the thermal cycling is mainly due to the delamination of the cathode. A delamination of the cathode leads to a significant increase of the ohmic resistance. The influence of the number of thermal cycles of a single cell was investigated and calculated by finite element method (FEM). Taking into account the electrolyte conductivity degradation rate at elevated temperatures and the measurements of the ohmic resistance of a whole single SOFC, the delaminated electrode area was estimated.

INTRODUCTION

Fuel cells are an attractive alternative for stationary energy production applications because of their high power generation efficiency. SOFCs have to fulfill several requirements, which mainly are a high electrical power output, long term stability and thermal cycling conditions. High electrical power output and high fuel efficiency was proven by several groups by applying thin electrolytes and intermediate layers (1,2). In this work, a SOFC was build, that shows a higher electrical power output and a better performance at thermal cycling conditions. A main part of the power losses in our planar Solid Oxide Fuel Cells (SOFCs) occurs due to the polarisation resistance of the cathode/electrolyte interface (3). The electrochemical reaction in a porous LSM-cathode is restricted to the three phase boundary (tpb) between cathode, oxidant and the electrolyte surface. Therefore, a decrease of the cathode resistance is achievable by an increase of the tpb or/and the effective electrolyte surface area (4). A decrease of the polarisation resistance and therefore an increase of the electrical output is possible by a three-dimensional penetration structure between cathode and electrolyte. A schematic sketch of the modified cathode is given in Figure 1. In the first part of this paper the preparation of SOFC-single cells with a modified ULSM-MOD cathode (ULSM: La deficient La₀.₇₅Sr₀.₂₅MnO₃) and the electrical measurements (I-V characteristics, impedance spectroscopy (IS)) are reported. The second part deals with the calculations of the delamination effects by FEM. FEM calculation has been carried out with regard to the electrical conductivities of the employed materials at elevated temperatures and by imple-
mentation of the geometrical size of the defects. The calculation of the detached electrode area by FEM provides an possibility to estimate the delaminated electrode area.

![Diagram showing standard and modified cathodes](image)

**Fig. 1** Scheme of a standard (left) and a modified (right) cathode. In case of the standard cathode, the tpb is restricted to the surface of the electrolyte substrate whereas the modified cathode exhibits a large amount of tpb's all over the structured electrolyte surface.

**EXPERIMENTAL**

Standard-type SOFCs were prepared by screen printing the anode (75 mol% Ni/8YSZ) and the cathode (ULSM: La-deficient strontium manganite $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$) on a 8YSZ-electrolyte and sintered at 1300 °C for 5 h.

SOFCs with a modified cathode were prepared using an 8YSZ-green tape (8YSZ: Tosoh TZ-8Y) which was covered with an appropriate 10YSZ-layer by screen printing. The covered substrates were sintered at 1550 °C for 1 hour. The sintered substrates had a size of 50 mm x 50 mm and a thickness of 200 μm.

In the next step the surface of the structured electrolyte was covered with a thin, nanoporous layer (approx. 80 nm thickness) consisting of La-deficient LSM (ULSM: $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$) which was applied by MOD (metal organic deposition). This method offers the advantage that metal-organic precursors can be dissolved to give coating solutions with a very high homogeneity at the molecular level. The metal organic precursors necessary for the preparation of the coating solutions are synthesised by using commercially available $\text{La}_2(\text{CO}_3)$, Mn(II)-Acetate and metallic Sr as starting materials. The synthesis is performed by reacting these components solely in the presence of propionic acid. After precipitation
and filtration the metalorganic precursors are then isolated as storable powders. To obtain pure perovskitic ceramic powders with the necessary composition, they were mixed in the target stoichiometry. The concentration of the coating solutions is typically adjusted between 11 wt% and 12 wt% oxide content. For the preparation by spin coating it is necessary to take the influence of the substrate and the various structure of sintered 8YSZ-particles into account to obtain a thin ULSM-layer which is homogeneous in thickness and composition. A subsequent heat treatment (170 °C / 15 min, 700 °C / 15 min, 900 °C / 15 min) leads to the oxidation of all organic moieties of the coating solution and to the formation of the oxide ceramic film with perovskite structure. These MOD-layers, which have been produced as dense or porous layers in a thickness range between 50 nm and 200 nm, exhibit a high electrical conductivity (5).

A conventional cermet anode consisting of a mixture of 75 % NiO and 25 % 8YSZ, was screen printed on the opposite side and sintered at 1350 °C for 5 hours. An ULSM-layer was screen printed onto the structured electrolyte, working as a current collector and gas distribution layer. This layer, consisting of larger ULSM-particles ($d_{50} = 3 \mu m$), exhibited a thickness of about 30 μm and a porosity of about 35 %, after sintering at 1000 °C for 2 hours.

The SOFC single cells were tested under realistic operating conditions using specially designed equipment. They were installed in an alumina-housing, the electrodes were contacted with a platinum-grid. The alumina-housing was located in a furnace which allows operating temperatures between 500 °C and 1000 °C.

An electronic load was used to adjust the current. The IS-measurements were performed using a SOLARTRON 1260 Frequency Response Analyzer in a frequency range from 100 mHz to 1 MHz. For the investigation of SOFCs by IS, a current amplitude $I_{amp} = 40 mA$ and $I_{bias} = 40 mA$ bias, under open circuit conditions (OCC), were applied.

The FEM calculations were carried out with the Maxwell software (6) taking into account experimental cell geometry and electrode arrangements (7). In each calculation an insulating surrounding atmosphere at the circumference of the sample was applied and the electrodes were considered as ideal electrical conductors ($\sigma > 10^5$ S/cm). The delamination area was included as defects which were applied into the FEM as a insulating patch with differing distance.

RESULTS AND DISCUSSION

A considerable increase of the power density is achievable in the single cells with modified cathode. Figure 2 shows I-V characteristics of single cells with different cathodes. The electrical power output was influenced directly by applying a three dimensional penetration structure for the cathode.

Different types of SOFCs were investigated in terms of their ability to withstand a series of thermal cycling. A thermal cycle not only consists of heating up and cooling down, in real operation the SOFC was electrically loaded between the individual thermal cycles. The SOFCs were thermally and electrically cycled to stress in particular the interface between cathode and electrolyte. In Table 1, the individual sequences of a thermal/electrical cycle is briefly shown.
Tab. 1 Procedure for a thermal cycle load

| STEPS                  | CONDITIONS |
|------------------------|------------|
| Heating up             | 20 °C→ 2 K/min → 950 °C |
| Hold time              | 5 h at 950 °C |
| Gas influx             | Anode 0.5 l/min N₂, cathode 0.5 l/min air |
| Reduction of the anode | Step by step increasing H₂/N₂-ratio |
| Impedance spectroscopy | 0.1→1·10⁶ Hz, I⁰ₙ₉₉ = 40 mA, Iₗₒ₉₉ = 0 A |
| Electrical load        | 0 A→0.0001 A/(cm²sec)→400 mA/cm² |
| Galvanostatic load     | 25 h |
| I-V characteristics    | Maximum current at 0.6 V cell voltage |
| Impedance spectroscopy | 0.1→1·10⁶ Hz, I⁰ₙ₉₉ = 40 mA, Iₗₒ₉₉ = 0 A |
| Electric load          | 0 A |
| Gas influx             | Anode 0.5 l/min 3:97 H₂/N₂, cathode 0.5 l/min air |
| Cooling down           | 950 °C→ 2 K/min → 20 °C |

I-V characteristics and AC-impedance were measured at standard- and modified ULSM-MOD-SOFC in between the thermal cycling. In Figures 3-5 the I-V characteristics and AC impedance with the different types of SOFC in dependence of the applied thermal cycles are shown.
Fig. 3 I-V characteristics of modified ULSM-MOD-SOFC from 1st up to 10th thermal cycle (TC) at 950 °C.

Fig. 4 AC impedance spectra of a modified ULSM-MOD-SOFC in dependence of the applied thermal cycles.
With increasing the number of thermal cycling, the electrical power output decreases. SOFCs with a modified structured ULSM-MOD-cathode show a significant higher durability in comparison to “standard” type SOFCs.

The thermal cycled SOFCs were afterwards investigated by SEM. The “Standard”-SOFCs cathodes were completely delaminated after only 5 times thermal cycling. SOFCs with structured ULSM-MOD-cathode showed a considerable better mechanical stability of the cathode due to the interlocking of YSZ-grains and porous cathode.

Considering the ohmic part of the IS, the enhancement in dependence of the applied thermal cycling could be influenced by the ageing of the electrolyte material and by the delamination of the electrode. The formation of secondary phases which may also affect the ohmic resistance was not considered in the model. FEM-calculations of cathode half cells were...
carried out. The calculations were made in dependence of the entire delaminated electrode area and the shape of the separated electrode. SOFCs with "standard"-type cathode show after thermal cycling great areas of delamination for every individual piece (see Figure 6 left). A completely different behaviour shows a SOFC with structured ULSM-MOD-cathode. The different delamination behaviour of the SOFCs were included into the FEM-calculations. A schematic sketch of the different delaminated areas is shown in Figure 7.

![Schematic sketch of different cathodes and their delamination behaviour. Left image "standard"-SOFCs after thermal cycling shows big areas of delamination. The interface with a three dimensional topology shows slight areas of delamination.]

To describe the cathode-area which was removed from the electrolyte, a FEM calculation was carried out in dependence of the cumulated delamination per electrolyte area and the length of every individual detached area. The ohmic resistance of a SOFC increasing directly, corresponding to the total delaminated area, when the delamination was singly connected. This is reasonable insofar, that the electrode has no electrical contact to the electrolyte. The correlation between the detached electrode and increasing ohmic resistance was not valid for small delaminated areas. The current density at the circumference of a delaminated area is higher in comparison to connected area. The FEM-calculations were carried out under the following assumptions:

| Tab.2 Material characteristics and geometrical sizes for FEM calculation |
|-----------------------------------------------|
| Conductivity in S/m | Thickness in μm |
|---------------------|-----------------|
| Cathode             | 10000           |
| Electrolyte         | 10              |
| Delamination        | 0               |
| Top/bottom electrode| infinity        |

The FEM-calculations were carried out by including the geometrical size of a cathode half cell and different shape of delamination occurring at the interface of cathode electrolyte. The whole delaminated area was in one case divided in equidistant parts (see Fig. 7) in the other case singly connected. Top- and bottom electrodes were applied at the cathode half cell and a voltage was applied. The net current was calculated by FEM. The ratio of the voltage and net current gives the ohmic resistance, which were afterwards compared to the ohmic resistance from the IS-measurements of SOFCs. Fig. 8 shows a wire mesh for a delaminated cathode half cell, were the calculations were undertaken which was included into the FEM. The mesh density was increased at the singularities at the circumference of the delaminated...
area, to get a consistent result of the current flow. The current density for the circumference of the delaminated area was higher compared to connected areas.

Fig. 8 Upper image: Calculation mesh of a cathode half cell with delamination; Lower image: Current constriction at delamination circumference, black → high current density, white → low current density

Fig. 9 FEM-calculation for the ohmic resistance of a cathode half cell in dependence of the cumulative delamination from 10% up to 75%.
The result of the calculations (Fig. 9) clearly show that the ohmic loss due to a delamination area which is separated in individual small pieces is considerably lower than the ohmic loss due to the same delamination for a single big piece.

The delamination behaviour in case of different type of cathodes ("standard" or structured ULSM-MOD-cathode) could be calculated by considering the degradation rate of the electrolyte material and the FEM results. The ohmic resistance degradation of a SOFCs is mainly influenced by the electrolyte material. The anode and the cathode show negligible decrease of the ohmic losses during operation (low fuel utilisation for the anode and air supply for the cathode side), therefore the whole ohmic loss occurs at the electrolyte. From the investigation of the ohmic losses of different SOFCs, delaminated electrode area can be estimated.

The FEM calculations for a SOFC with a structured ULSM-MOD-cathode show, that an increase of delaminated electrode area leads only to a slight increase of the ohmic resistance (see Fig.9). The evaluated delamination area using FEM showed no good correlation with the results obtained by SEM, because of the slight differences of ohmic resistance and the measurement error. The ageing of the 8YSZ-electrolyte material, evaluated at a similarly 8YSZ specimen, resulted in a decrease in ionic conductivity which leads to a significant error for the FEM calculated cathode delamination.

The calculations for a standard-SOFC under thermal cycling conditions show reasonable results. The calculations of the delamination of a 5 times thermal cycled standard SOFC was carried out under consideration of the ageing effects (loss of ionic conductivity) of the electrolyte material. In Table 3 the ohmic resistance of a whole SOFC and the calculations of the delaminated electrode area is shown.

**Tab.3 Calculations of a delaminated cathode area in dependence of the number of thermal cycles**

| Thermal cycle | Op. Time [h] | Measured resistance [mΩ·cm²] | Ageing of the electrolyte $\sigma$ (950 °C, 0 h) = 13,3 S/m [mΩ·cm²] | Correction of the ohmic resistance due to electrolyte ageing [mΩ·cm²] | Delaminated electrode area [%] |
|---------------|-------------|------------------------------|-------------------------------------------------|----------------------------------------------------------------|-----------------------------|
| 0             | 0           | 300                          | 13,30                                           | 300,7                                                          | 0%                          |
| 1             | 140         | 390                          | 12,67                                           | 315,7                                                          | ~ 40%                       |
| 2             | 280         | 470                          | 12,02                                           | 332,7                                                          | ~ 50%                       |
| 3             | 420         | 540                          | 11,50                                           | 347,7                                                          | ~ 57%                       |
| 4             | 560         | 650                          | 11,02                                           | 362,8                                                          | ~ 62%                       |
| 5             | 700         | 750                          | 10,64                                           | 375,9                                                          | ~ 73%                       |

The FEM-calculations were made under the assumption that the delamination occurred in a piece (see Figure 6 left). The investigation of the real delaminated area could be carried out only after operation of the SOFC using SEM. If the delamination behaviour of an electrode is known, the total delaminated area can be calculated by FEM.
CONCLUSIONS

Single cells were thermal-cycled and electrical measurements (i.e. I/V-curves, impedance spectroscopy) were performed at operation conditions (950 °C, anode: H₂, 0.5 l/min, cathode: air, 0.5 l/min, electrode area: 10 cm²). An increase of the ohmic resistance of the single cells obtained by impedance spectroscopy was caused by the thermal cycling, which provoked a delamination of the cathode, and the ageing of the electrolyte material. A FEM-procedure was developed to estimate the delaminated electrode area of the cathode. The FEM-calculations were made under the assumptions, that an increasing ohmic resistance was influenced by the delamination of the cathode and the ageing of the electrolyte.

The FEM calculations showed that the shape of delamination plays an important role for the entire ohmic resistance of a SOFC. The current density of the delamination-circumference is higher compared to well connected cathode areas, therefore the total ohmic resistance was lower for a lot of distributed small pieces of delamination.

Single cells with a modified cathode were able to resist more thermal cycles compared to single cells with a screen printed single layer cathode, because the interlocking of YSZ-grains within the cathode structure prevented an extensive delamination.

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