Nondestructive cell evaluation techniques in SOFC stack manufacturing

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ABSTRACT

Independent from the specifics of the application, a cost efficient manufacturing of solid oxide fuel cells (SOFC), its electrolyte membranes and other stack components, leading to reliable long-life stacks is the key for the commercial viability of this fuel cell technology.

Tensile and shear stresses are most critical for ceramic components and especially for thin electrolyte membranes as used in SOFC cells. Although stack developers try to reduce tensile stresses acting on the electrolyte by either matching CTE of interconnects and electrolytes or by putting SOFC cells under some pressure – at least during transient operation of SOFC stacks ceramic cells will experience some tensile stresses.

Electrolytes are required to have a high Weibull characteristic fracture strength. Practical experiences in stack manufacturing have shown that statistical fracture strength data generated by tests of electrolyte samples give limited information on electrolyte or cell quality. In addition, the cutting process of SOFC electrolytes has a major influence on crack initiation.

Typically, any single crack in one the 30 to 80 cells in series connection will lead to a premature stack failure drastically reducing stack service life. Thus, for statistical reasons only 100% defect free SOFC cells must be assembled in stacks. This underlines the need for an automated inspection. So far, only manual processes of visual or mechanical electrolyte inspection are established. Fraunhofer IKTS has qualified the method of optical coherence tomography for an automated high throughput inspection. Alternatives like laser speckle photometry and acoustical methods are still under investigation.

Keywords: SOFC, cell, stack, stresses, testing, quality, inspection methods

1. INTRODUCTION

High temperature fuel cells are considered as one of the most promising technologies for energy conversion in the 21st century. Due to the high efficiency and the versatility of the technology, the Solid Oxide Fuel Cell (SOFC) or its reversed use the Solid Oxide Electrolyze Cell (SOEC) are favored by many commercial and academic developers.

All concepts base on the combination of a defined number of smaller cells (planar, tubular or mixed design) to a larger cell assembly, the“stack”, for getting higher voltages and/or currents than from a single cell. Typically, up to one or in best case several kW electric DC power will be generated in a single SOFC stack. Several stacks can be combined again to larger systems or stack modules up to several 100kW.

The SOFC stack is the key technology in the value chain from ceramic powders over cells to stacks and SOFC systems for different applications like industrial CHP systems, micro-CHP systems or off-grid power generators.

The following article focusses on the example of planar stacks where 20 to 80 planar SOFC or SOEC cells are combined electrically in series connection and in a fluidic parallel mode to a single SOFC or SOEC stack. The findings can be transferred in principle to other stack designs as well.

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2. SOFC CELL MANUFACTURING

SOFC cells, sometimes called Membrane Electrode Assemblies (MEAs), represent the electrochemical active component in the SOFC stack. The most popular versions of SOFC cells are electrolyte supported or anode supported, that means the electrolyte or the anode is the thickest and first layer giving structural integrity to the cell. Manufacturers like BloomEnergy, Viessmann/Hexis, Sunfire or Fraunhofer IKTS use electrolyte supported cells (ESC) in contrast to anode supported cells (ASC) favored by Versa Power or Solid Power.
The basic manufacturing process for ESC cells is outlined in Fig. 1 below:

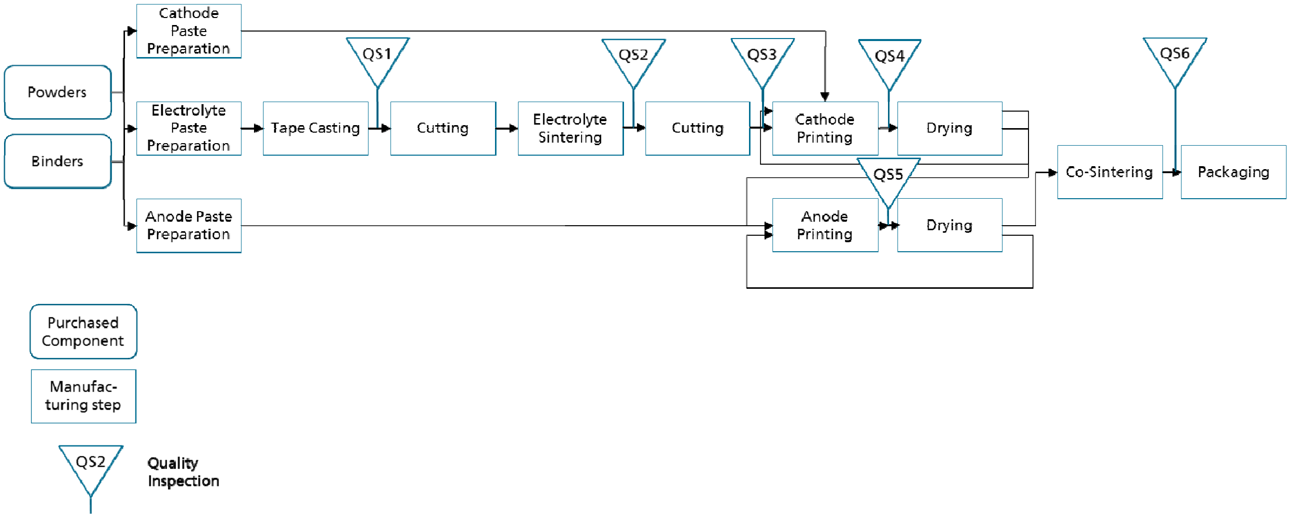
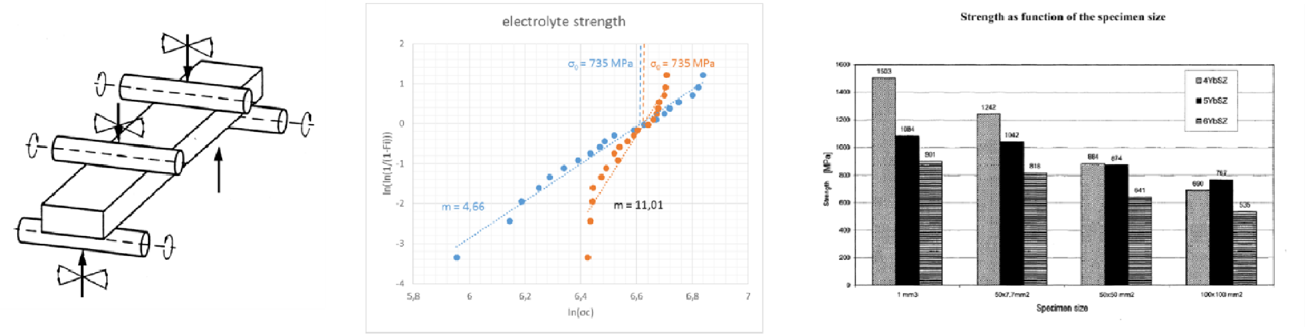


Figure 1.Basic manufacturing steps of an electrolyte supported SOFC cell

During the tape casting, drying and sintering steps a high initial strength of the electrolyte, a fine and defect free bulk structure as well as a smooth surface structure is targeted. For ESC cells the total resistance is strongly dependent on the ohmic resistance of the relative thick electrolyte (typically 40-120 µm). Therefore, thinner electrolyte sheets offer significant cost and performance advantages while showing the same material strength.
The realized mechanical strength of each electrolyte sheet batch manufactured can be measured by a destructive statistical test method like four-point-bending test, a ring on ring or ball on 3 ball test. The characteristic strength data measured have to be corrected to realistic sample sizes and low failure probabilities as well as high operating temperatures under humid atmospheres prevailing in SOFC stacks.

Highest electrolyte inert strength data are reached for 3YSZ up to 800MPa[3] (ZrO_2 with 3mol% Y_2O_3) and lowest about 200MPa[2,6] for 10Sc1CeSZ and below 100MPa[6] for 8YSZ. Weibull modulus m is typically 10-12 in a good manufacturing batch while Weibull moduli smaller than 8 are inacceptable. A high Weibull modulus for any cell manufacturing batch is even more important than a high mean strength for high cell reliability as illustrated in Figure 2.



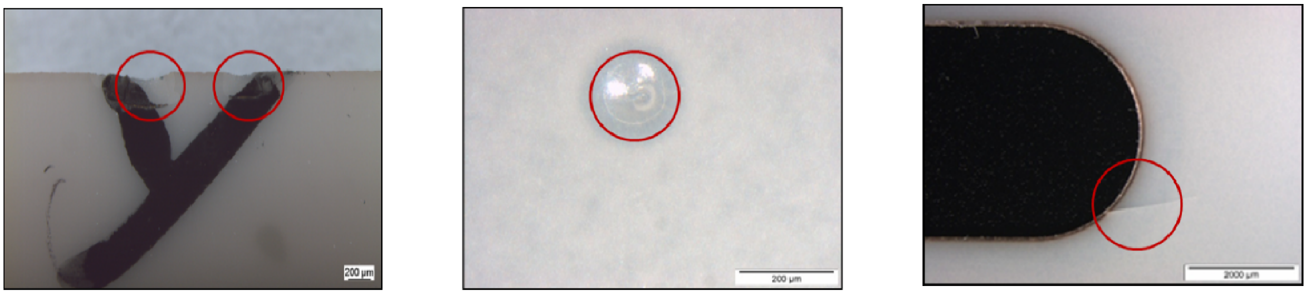
a) Four point bending test

b) Double logarithmic Weibull plot
m - Weibull slope
σ_0 - Mean Strength (63.2% of specimens break)

c) Size dependance

Figure 2. Weibull plot of electrolyte sheet bending strength data

Sub-critical crack growth is another phenomenon to be considered in evaluation of SOFC cell strength and reliability. It means that cracks grow slowly at the crack tip well below the critical stress threshold value due to chemical corrosion effects. For 3YSZ it is proven that water or moisture in the atmosphere is the main contributor to sub-critical crack growth. Thus, any defect of the smooth electrolyte surface is inacceptable.



a) edge spallation

b) pinholes

c) cracks

Figure 3. Pictures of typical defects in electrolyte sheets

Typical failures in SOFC cells include pinholes, edge spallations and cracks. Case c) in Fig. 3 above shows the very typical situation of a crack initiated by laser cutting of internal gas manifold holes.

As gas separation between anode and cathode side is essential for a stable and durable stack operation, any type of these failures causing even small leakages will lead to premature stack failure. Gas leakages can be detected by the leakage test shown in Fig. 5 below.

Most critical in cell manufacturing is the final cutting step of the hard, sintered electrolyte sheet. The quality inspection step QS3 acc. to Fig.1 therefore has the highest priority with regard to electrolyte defects. Beside thickness measurement, area related weight measurement and potentially optical inspection using imaging techniques no automated quality inspection is known so far.

In prototype manufacturing, stack manufacturers typically apply extensive manual optical inspection or even some types of proof bending tests in a 100% inspection regime.

3. SOFC STACK DESIGN, ASSEMBLY AND QUALITY CHECKS

One of the key objectives in SOFC stack design is to avoid any mechanical tensile and shear stresses on ceramic SOFC cells. As SOFC stacks are experience thermal cycles between room temperature and plus 800°C (or even higher during joining), this requires a careful material selection that limits possible combinations of metals and ceramics. A good match in the thermal expansion coefficients of the components or materials is required. For this reason, either a combination of fully stabilized 10Sc1CeSZ electrolytes with FeCr powder alloys (>75% Cr) or a combination of partially stabilized electrolytes 3YSZ or 4YbSZ with ferritic steels like CroferH alloy has proven most practical.
If the thermal expansion of the metal component is slightly higher than that of the electrolyte, the cell, embedded in viscous glass sealings under operation temperature, becomes fixed by cooling down under the glass transition temperature of the seal. So the cell becomes preloaded. To prevent buckling, some axial pressure on the stack is required to maintain the stability of the stack under room temperature. Due to the compressive stress acting on ceramic cells the stack is inherently more robust against tensile stresses in the lower temperature range.

The basic manufacturing steps for a SOFC stack are described below:

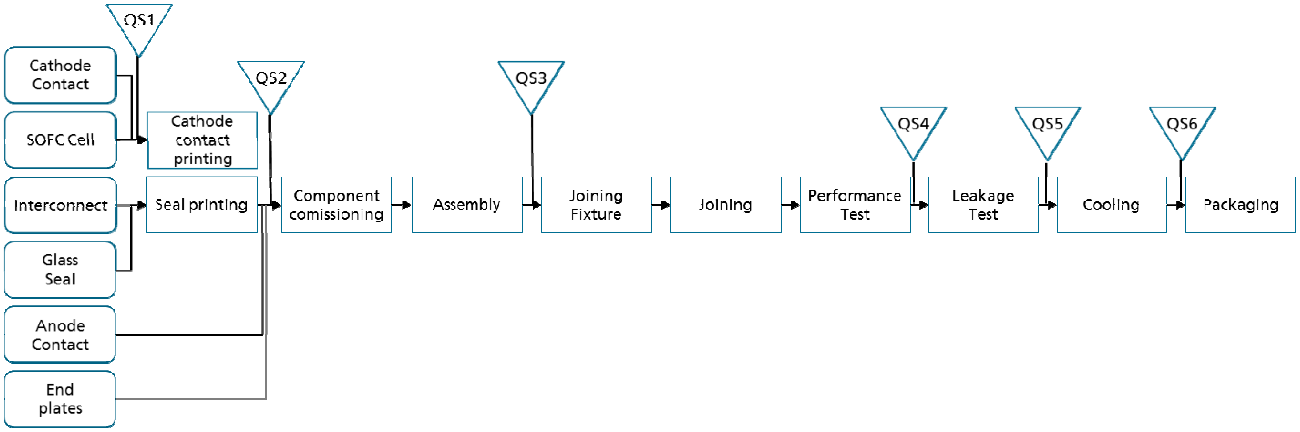


Figure 4. Basic manufacturing steps for planar SOFC stacks (ESC cells)

It should be noted that a leaky cell (typically caused by a sealing failure or a crack in the electrolyte) can be detected earliest in QS5 (electrochemical leakage test). Fig. 5 shows the typical characteristic of a cell fracture in the electrochemical leackage test before QS5 in stack manufacturing. This non-destructive test method had been applied successfully in stack manufacturing.

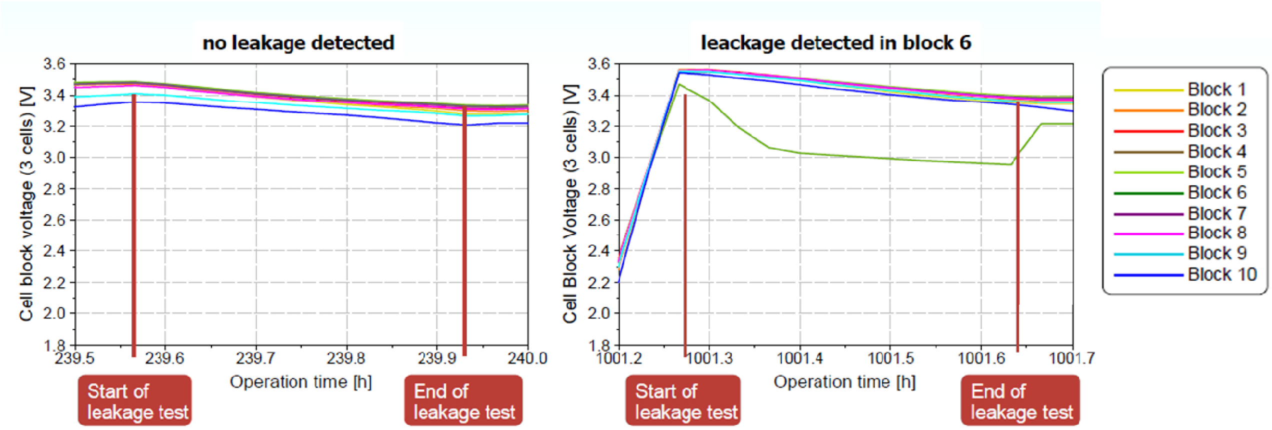


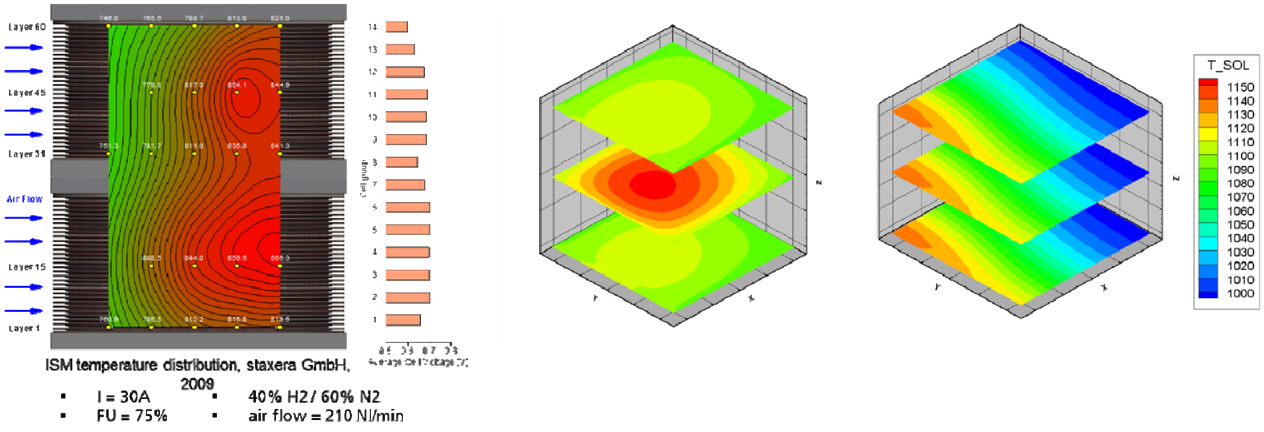
Figure 5. Detecting a cell fracture in block 5 by a leckage test after stack joining

Any single cell failure, not detected in QS3 or QS6 of previous cell manufacturing steps, can be detected only at this point again. At this time however, 100% of stack manufacturing cost are spent already and the failure will result in a scrap loss of the complete stack. The cost of any single undetected cell failure will have increased by the factor 100 or more. Not surprisingly, cost projections for SOFC systems show the highest sensitivity for cell and stack production yield rates[9].

This means, intensive electrolyte screening before and after electrode printing is really worthwhile.

4. STRESSES ON SOFC CELLS IN STACK OPERATION

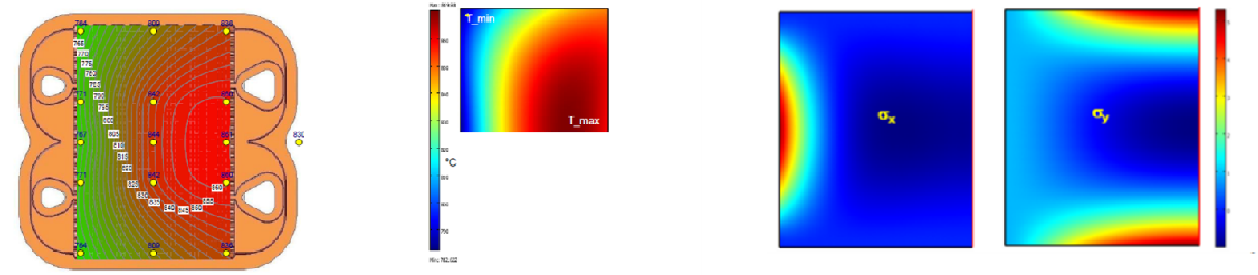
In theory, electrolyte strength data given in chapter 2 above should be more than adequate to ensure a good robustness of electrolyte supported cells during stack operation. However, the air cooled SOFC cell will face a strong non-isothermal situation under load and in transient operating conditions.



a) Thermal map of an SOFC stack in operation[1] b) Overheated stack (simulated) c) cooled stack (simulated)

Figure 6. Thermal situation a) measured in full power situation[5] and simulated for critical stack operation modes.

The case b) “overheated stack core without adequate cooling” shown in Fig. 6 above will result in a local mechanical extension of components in x-y cell plane causing cell buckling, contact loss and finally cell fracture. The case c) in Fig. 6 is the standard thermal situation for steady-state stack operation.



a. **Measured temperature distribution in single a stack layer**

b. **Adjusted temperature distribution in the layer FEA model**

c. **Calculated stresses in the FEA model for any measured temperature distribution**

Figure 7. Simulated stress pattern in a SOFC cell for a measured temperature profile during stack operation

Based on these simulations, it is estimated that tensile stresses up to 80 and 100 MPa may occur under conditions discussed above during thermal cycling. It becomes clear that these stresses are already critical with respect to electrolyte strength data shown above.

By considering the effects of sub-critical crack growth the situation becomes more dramatic. Fleischhauer et al[7] have calculated the electrolyte strength with 100 MPa at 850°C and 150 MPa at room temperature for a failure probability 1E^{-5} in 100 cm^2 loaded cell area.

Due to the serial connection of cells the stack failure probability calculates $P_{Stack} = 1 - (1 - P_{cell})^n$, that means for n=60 cells the stack failure probability is about 60 times higher than for a single cell. Thus, any crack or cell flaw, where sub-critical crack growth may be initiated, should be avoided.

5. METHODS FOR AUTOMATED NONDESTRUCTIVE CELL INSPECTION

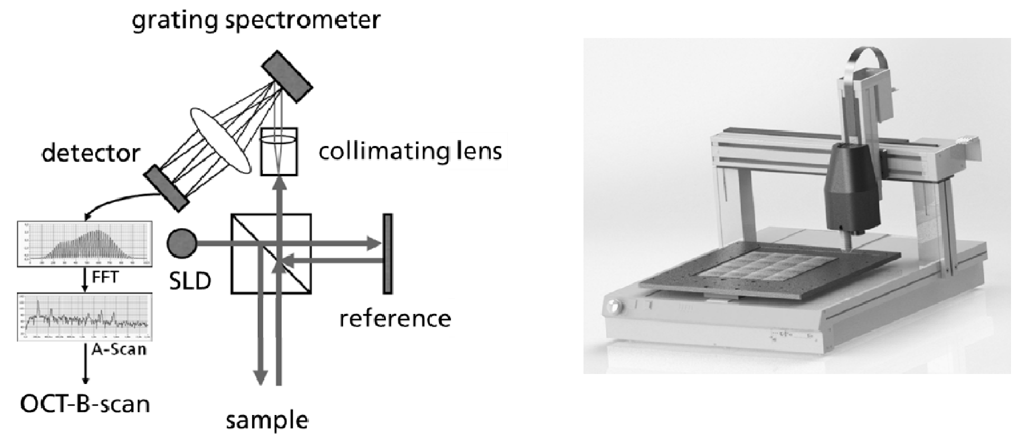
In chapters 2 to 4 above it is explained, why an automated inspection of SOFC electrolytes and cells is an essential step for the successful commercialization of the technology. The inspection should eliminate cells with cracks of failures early in the production process to maximize Weibull coefficient of cell strength, eliminate failures like bumps causing local stress concentrations in the pressed cell and eliminate pinholes or spallations where the electrolyte becomes exposed to humid atmospheres accelerating sub-critical crack growth.

The key requirements for the industrial use of such an inspection method are:

a. Inspection time per cell / sheet < 3s (assuming a production volume of 10MW/a)
b. No vacuum method
c. Non-contacting measurement or at least no additional mechanical or thermal stress burden
d. No contamination with fluids or particles

Based on the list of requirements above optical, acoustical or electromagnetic NDE inspection methods are preferred. Fraunhofer IKTS is using two optical methods using the direct interaction of light and material and thus going beyond image processing.

These methods are optical coherence tomography (OCT) and Laser Speckle Photometry (LSP). Both methods have a different focus and are explained below. They are limited to surface near defects, what is less a problem for thin planar objects like SOFC cells.

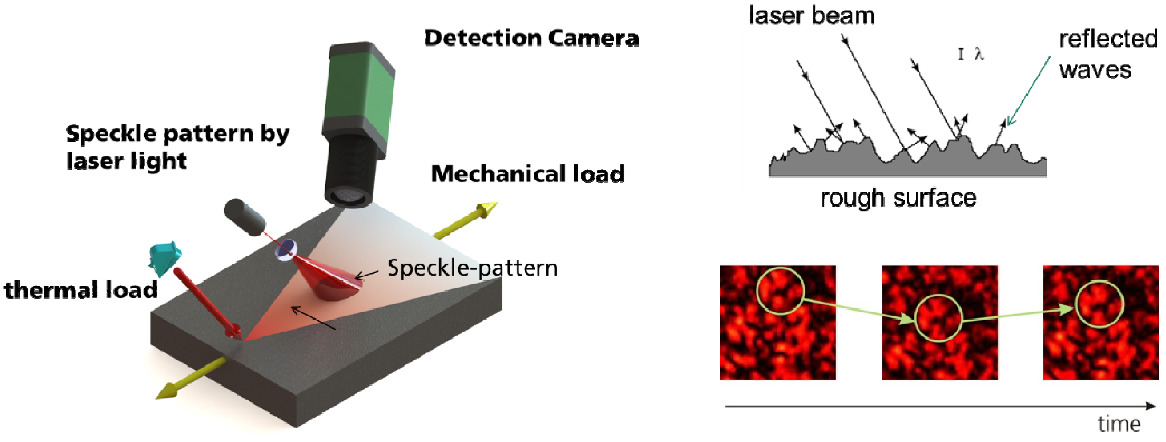


a) optical setup

b) scanning system

Figure 8. Industrial OCT system

The optical coherence tomography is an echo technique like Ultrasonics. The industrial OCT system in Fig. 6 is showing a Fourier-Domain OCT-System with a shortwave coherent light source (broadband super-luminescence diodes SLD) of central wavelengths from 900nm to 1300nm. The diode light source is split in a reference and a sample arm. The interference between both arms processed by fast fourier transformation (FFT) gives the depth-reflection-profile of reflecting elements in the sample (A-Scan). A lateral sequence of A-scans results in a B-scan. Lateral movements in two directions generate a tomogram (3D) as a sequence of B-Scans. The current velocity of the system is 30 B-scans per second with a resolution of 20 microns. A complete 3D tomogram may take up to 6 minutes. This is still by factor of 10 to 20 too slow if the complete cell has to be scanned. The focus on critical areas, a smaller resolution and the combination with optical image processing could help reducing the inspection time. Estimated OCT inspection time is in the range of scanning acoustic microscopy, however OCT has the advantage to operate without a coupling fluid.



a) schematic setup

b) Speckle pattern dynamics

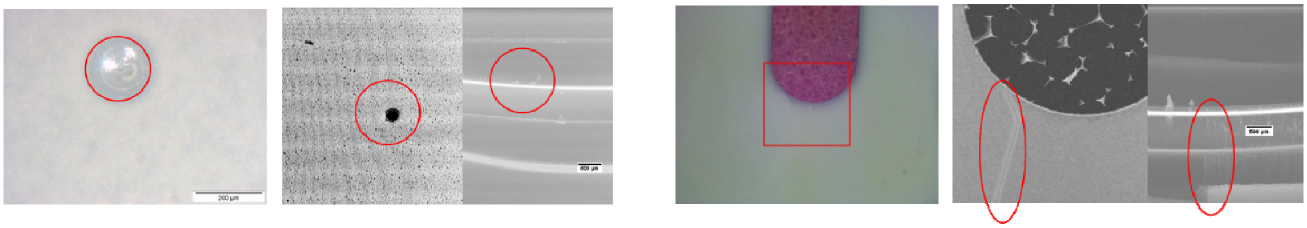
Figure 9. Laser Speckle Photometry

Time-resolved laser-speckle photometry (LSP) is a new technique based on the analysis of the temporal variation of speckle patterns that develop in mechanical or thermal stimulations of the test object. The stimulation can be initiated either by the process itself or by an additional introduction of heat or mechanical stress during the testing process. Moreover, it is possible to characterize surfaces on the basis of static speckle patterns.

The change in thermal diffusivity measured by the variation of the speckle pattern can be analyzed by a set of mathematical methods. The measured data correlate with mechanical and structure parameters like hardness, porosity or stresses. Measuring time depends on heat up / stimulation time and is typically less than a second. Data processing is depending on computer power available but takes less than a minute.

6. PRELIMINARY RESULTS

The methods shown above have been applied to SOFC cells used for stack assembly at Fraunhofer IKTS.

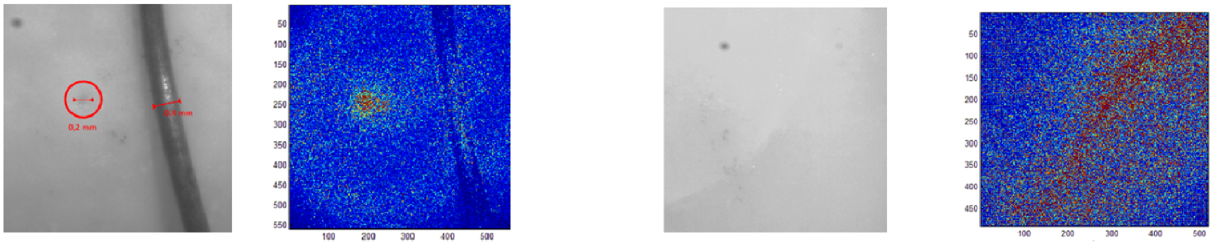


a) Pores in ceramic electrolytes

b) cracks in ceramic electrolytes

Figure 10. Crack Detection capability by OCT

In the case of OCT Fig. 10 reveals that depending on the defect type both the A-scan picture or the top view can deliver better results.



a) Pores in ceramic electrolytes

b) cracks in ceramic electrolytes

Figure 11. Pores and cracks in a ceramic electrolyte detected by LSP

Both methods, Optical Coherence Tomography (OCT) and Laser Speckle Photometry (LSP), have shown the capability to detect holes and cracks, barely visible, in planar ceramic electrolytes used for electrolyte supported cells (ESC). The automated processing, failure classification and automated decision making still has to be developed before the methods may be applied industrially. The comparison of the methods OCT and LSP in table 1. below is summarizing the technical parameters, advantages and limitations.

Table 1. Status of Technology readiness and application focus of OCT and LSP for SOFC cell testing

Parameter	OCT	LSP
Preferred inspection parameters	• Cracks, failures	• Integral Porosity, material composition • Cracks and other failures • stresses
Advantages	Easily compatible with optical inspection	Several parameters can be evaluated in parallel
Limitations	Method is only applicable for light and translucent materials Failure catalogue required	Selection of stimulation and calibration of the method for any component / material required
Resolution and penetration depth	Flexible up to <10µm 3-5mm	10µm Low, depending on parameter and stimulation
100% testing time 10x10cm cell	1 to 3 min/cell	< 1min /cell
Manufacturing process integration	Separate measuring station	Simple and flexible even in existing processes
Technology readiness	TRL 6 in Industrial NDE	TRL 5 in Industrial NDE

7. SUMMARY & CONCLUSIONS

Thermal and mechanical robustness of SOFC cells and stacks had been a challenge in SOFC technology development for a long time.

Over the last 10 years, SOFC Stack developers and cell manufacturers have learnt how to optimize the SOFC stack design and operation regimes to reduce critical thermal and mechanical stresses to values below 120 MPa while using high strength electrolytes, able to tolerate these stresses. This was a key steps towards SOFC stacks offering frequent cycling capability.

Based on the statistical and practical risk of stack failures in production or early operational life due to cell imperfections, a 100% inspection of electrolytes and SOFC cells is inevitable. The preferred position in the manufacturing sequence of stacks is after cutting of the final cell shape from sintered electrolytes and again after printing electrodes and co-sintering or before the start of the stack manufacturing process. Industrial methods beyond visual inspection are not established yet[9]. Even a failure rate of 1% would results in yield rate loss of 200.000 € in stack production at projected volume production cost of 2.000 €/kW and (low) 10 MW per year production rate. Furthermore, an automated electrolyte inspection is required to push the stack failure rate due to cell fracture down to single ppm levels over the stack lifetime.

In this paper two innovative optical methods based on the interaction of light with the electrolyte or electrode material are proposed. Initial results show that the detectability of typical defects by both methods is good while the automated industrial solution still has to be developed.

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