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 fuel cells and other stack components leading to reliable long-life stacks is the key for the commercial viability of the SOFC 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 fracture strength data generated by ball-on-ring 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 cell crack in one the 30-80 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 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 connection of a limited number of smaller cells (planar, tubular or mixed design) to a larger cell “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. 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 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 design concepts as well.
2. SOFC CELL MANUFACTURING

SOFC cells (sometimes called Membrane Electrode Assemblies (MEAs)) represent the electrochemical active component in the SOFC stack. 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:

During the tape casting, drying and sintering steps a high initial strength of the electrolyte, a fine and defect free structure as well as a smooth surface structure is targeted. For ESC cells the total resistance is strongly dependent from the ohmic resistance of the relative thick electrolyte (typically 40-120 µm). Therefore thinner electrolyte sheets offer significant cost and performance advantages. The realized mechanical strength of each electrolyte sheet batch manufactured can be measured by a destructive 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 and humid atmospheres prevailing in SOFC stacks.

Highest electrolyte inert strength data are reached for 3YSZ up to 800MPa3 (ZrO2 with 3mol% Y2O3) and lowest about 200MPa6 for 10Sc1CeSZ and below 100MPa6 for 8YSZ. Weibull modulus m is typically 10-12 in a good manufacturing batch while Weibull modulus smaller than 8 are inacceptable. A high Weibull modulus for any cell manufacturing batch is as important as or even more important than high material strength for a high reliability as illustrated in Figure 2.

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

Figure 2. Weibull plot of electrolyte sheet bending strength data
Sub-critical crack growth is another phenomenon to be considered in evaluation SOFC cell strength and reliability. It means that cracks growth 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 unacceptable.

Typical failures in SOFC cells include pinholes, edge spallation 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 for the hard sintered electrolyte sheet, thus quality inspection step QS3 acc. to Fig.1 has the highest priority with regard to electrolyte defects. Beside thickness measurement, potentially optical inspection by imaging techniques and area related weight measurement no automated quality inspection is known so far.

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

### 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 have are suffering thermal cycles between room temperature and plus 800°C (or higher during joining) this requires are careful material selection and limits the combination of metals and ceramics. To ensure a good match in the thermal expansion coefficient between 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 the electrolyte the cell is embedded in viscous glass under operation temperature and fixed by cooling down under the glass transition temperature while the cell will be preloaded. Axial pressure on the stack is required to maintain the stability of the stack under room temperature for this reason. Due to the compressive stress acting on ceramic cells the stack is inherently robust by design.

The basic manufacturing steps for a SOFC stack are described below in Fig. 4:
It should be noted that a leaky cell can be detected earliest in QS5 (electrochemical leakage test) if any failure hadn’t been detected in QS3 or QS6 of cell manufacturing operations.

Fig. 5 shows the typical characteristic of a cell fracture in the electrochemical leakage test before QS5 in stack manufacturing. This non-destructive test method had been applied successfully in stack manufacturing. At that time however, 100% of stack manufacturing cost are spent already and failure will result in a scrap loss of the complete stack manufacturing cost. Not surprisingly cost projections for SOFC systems show the highest sensitivity for cell and stack production yield rates. This underlines the need for intensive electrolyte screening before and after electrode printing.

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 in stack operation. However, the air cooled SOFC cell will realize a strong non-isothermal situation under load and in transient operating conditions.
The case b) - overheated stack core without adequate cooling - shown in Fig. 5 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 case for stack operation.

Based on these simulations it is estimated that tensile stresses in the range between 100 and 150 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 discussed above.

Considering the effects of sub-critical crack growth the situation becomes more dramatic. Fleischhauer et al have calculated the electrolyte strength with 100 MPa at 850°C and 150 MPa at room temperature for a failure probability in 100 cm² loaded area. Thus any crack or cell flaw where sub-critical crack growth may be initiated must be avoided.

5. METHODS FOR AUTOMATED NONDESTRUCTIVE CELL INSPECTION

From chapters 2 and 3 of this paper one can clearly conclude that an automated inspection of SOFC electrolytes and cells is required for the successful commercialization of the technology.

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 has built competencies in 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). These laser based methods have a different focus and are explained below. Both methods are limited to surface near defects, what is less a problem for thin planar objects like SOFC cells.

Figure 8. Industrial OCT system

The optical coherence tomography is an echo technique similar to 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 900 to 1300nm. The diode light source is splitted in a reference and sample arm, and 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 or by lateral movements in two direction we see a tomogramm (3D) by a sequence of B-Scans. The current velocity of the system is 30 B-scans per seconds with a resolution of 20 microns. A complete 3D tomogram thus takes about 6 minutes. This is still factor 10 to 20 too slow. The inspection time is in the range of scanning acoustic microscopy, however OCT has the advantage to operate without a coupling fluid.
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 objects. 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.

Figure 10. Crack Detection capability by OCT
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 150 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 start of stack manufacturing process. Industrial methods beyond visual inspection are not established yet. 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.

In this paper two innovative optical methods based on the interaction of light with the electrolyte or electrode material are proposed. Although none of the methods alone will solve the challenge to establish an automated inspection process with automated rejection of failed parts a combination of the methods including optical image processing is proposed. Initial results show that the detectability of typical defects can be improved.

REFERENCES