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Strength of an electrolyte supported solid oxide fuel cell

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HIGHLIGHTS

- Strength of a SOFC is described regarding temperature, ageing and electrodes.
- Both electrode layers substantially weaken the strength of the electrolyte.
- The cell is weakest at its anode side at operating temperatures.
- Sub-critical crack growth does not further weaken the cell strength.
- Residual stresses are of less importance regarding the overall strength minimum.

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ABSTRACT

For the proper function of solid oxide fuel cells (SOFC) their structural integrity must be maintained during their whole lifetime. Any cell fracture would cause leakage and partial oxidization of the anode, leading to a reduced performance, if not catastrophic failure of the whole stack.

In this study, the mechanical strength of a state of the art SOFC, developed and produced by Hexis AG/Switzerland, was investigated with respect to the influence of temperature and ageing, whilst for the anode side of the cell the strength was measured under reducing and oxidizing atmospheres.

Ball-on-3-Ball bending strength tests and fractography conducted on anode and cathode half-cells revealed the underlying mechanisms, which lead to cell fracture. They were found to be different for the cathode and the anode side and that they change with temperature and ageing. Both anode and cathode sides exhibit the lowest strength at T = 850 °C, which is greatly reduced to the initial strength of the bare electrolyte. This reduction is the consequence of the formation of cracks in the electrode layer which either directly penetrate into the electrolyte (anode side) or locally increase the stress intensity level of pre-existing flaws of the electrolytes at the interface (cathode side).

1. Introduction

Solid oxide fuel cells (SOFCs) are state of the art ceramic based components, to convert chemical energy of many different fuels into electrical energy. The electrical efficiency of the underlying electrochemical conversion process can reach up to 70%. One requirement for these high levels of efficiency is the physical separation of the fuel from the oxidizing air, through the gastight electrolyte. This ensures that the fuel is not directly burned off. Any kind of leakage reduces the amount of effectively utilizable fuel and therefore causes lower efficiency.

One way for leakage to occur in a SOFC system is when the electrolyte fractures and the gas tightness is no longer maintained. Hence the mechanical reliability of the electrolyte as part of the cell has to be ensured during the whole time of operation; including thermo and red-ox cycles.

One approach is to keep possible tensile stresses acting on the cell to a minimum. This can be done, for instance, by proper

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thermal management, in order to reduce the thermal stresses that are caused by inevitable thermal gradients over the cell area [1]. Another way is to select the electrodes and the electrolyte in a way, so that the strength of the cell and the corresponding reliability is sufficiently large. An overview over the mechanical properties of several gadolinia-ceria and zirconia electrolytes can be found in Refs. [2–4]. Beside the properties of the electrolyte, the robustness of the cell is further determined by the properties of the electrodes and their interphases or interfaces, respectively. In previous studies it has been reported that cracks within the electrodes may extend into the electrolyte, thus weakening its strength [5–7]. This damage process is either promoted by residual stresses or when an external tensile stress is applied to the electrode.

In the present study the robustness and the reliability of a state of the art electrolyte supported SOFC is investigated, which was provided by Hexis AG (Winterthur, Switzerland). The cell is characterised by an initial power output of 22 W, when supplied with 4 g/h of partial catalytic reformed natural gas per cell (corresponds to 52 W), operated at 0.7 V cell voltage and 850 °C. The steady state power degradation at a constant voltage operation is 0.7%/1000 h [8]. This cell is employed in the current Hexis μ-Combined-Heat-and-Power-Plant, the Galileo 1000 N. Further information about the stack and system is also given in Ref. [8]. Here the cell has to endure any given mechanical load being operated at 850 °C, while being subjected to reducing and oxidising atmospheres for up to 40,000 h and several thermo red-ox cycles (on–off cycles). In order to take these different aspects into account, Ball-on-three-Balls (B3B) bending strength measurements have been performed on cathode and anode half-cell specimens covering the whole relevant temperature range from room temperature up to 850 °C, whilst the anode half cells were tested either in their reduced or oxidized state. Possible ageing effects are investigated by testing half-cells obtained from cells, which were continuously operated for up to 12,000 h.

2. Experimental

2.1. Specimens

The SOFC from Hexis consists of five layers as shown in Fig. 1. The anode is a bilayer with a 30 μm thick current collector (A2) consisting of a porous NiO (70 wt.-%)-$Ce_{0.6}Gd_{0.4}O_2$ (30 wt.-%) cermet and a 10 μm thick functional layer (A1) comprised of the same cermet but with 50% NiO content. The electrolyte is a dense 6 mol-% Sc_2O_3 stabilized ZrO_2, with a thickness of 160 μm. The cathode is again a porous bilayer with a 60 μm thick $(La_{0.78}Sr_{0.2})MnO_{3-\delta}$ current collector (C2) and a 15 μm thick functional layer (C1) comprised of a $(La_{0.78}Sr_{0.2})MnO_{3-\delta}$ (50 wt.-%)-Y_2O_3(8 mol %)-ZrO_2 (50 wt.-%) composite.

The electrolyte is produced via a tape casting route. Therefore it possesses two surfaces, one which was in contact with the supporting foil, where it was cast onto and the opposite side, which was in contact with the doctor blade. As the supporting foil has a structured surface, the respective electrolyte exhibits a rougher topography than the other side of the tape after sintering. In order to study the influence of the different roughness, two different cells were investigated: a cell, where the anode was screen-printed onto the rough side, which marks the standard case and one where it was printed onto the smoother side.

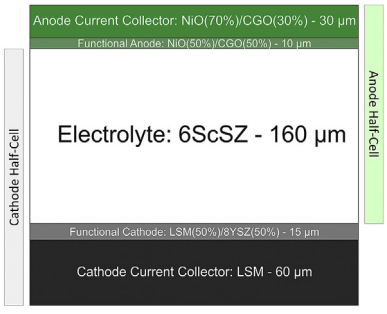

Fig. 1. Principle architecture and composition of the Hexis SOFC.

The samples for the B3B bending tests were prepared by cutting the cells with a diamond wheel saw into 4 × 3 mm^2 rectangular plates, while gluing them onto a support foil. The cutting speed was adjusted, so that no cracking occurred at the samples edges, which was checked via light microscopy. Any possible effect of micro cracks, which might have not been detected and having a length smaller than 10 μm, is neglected, as the B3B bending test just loads the samples centre with tensile stress, while the edges are compressed [9,10]. Also, this way of sample preparation has been successfully applied to glass substrates, which are even more delicate to handle due to their low fracture toughness [11].

The actual testing was performed on half-cells, where both cathode layers of each specimen were gently polished off to obtain the anode half-cells and vice versa to obtain cathode half-cells (see Fig. 1). The advantage of these samples is that it simplifies the stress analysis. Furthermore the potential uncertainties regarding the description of the elastic response of these heterogeneous multilayers, which is necessary for stress analysis, is reduced to minimum.

2.2. Biaxial bending strength testing

The biaxial strength was determined using the Ball-on-three-Balls (B3B) test [9,10,12], where plate like specimens can be tested in biaxial flexure. Details of the testing procedure can be found elsewhere [13]. For the testing of the 4 × 3 mm^2 sized specimens 2.2 mm balls were chosen. The three balls were arranged below the sample, supporting it, while the loading ball was on top of the sample as described in Ref. [3]. All tests were performed in a dry atmosphere in order to avoid possible "environmental assisted cracking", as found in this type of material [4]. At room temperature (RT) tests were made in an Argon atmosphere. Samples that should remain in their oxidized state were tested in a mixture of Argon(80%)/Oxygen(20%), while forming gas (5% H_2/95% N_2) was used to reduce two sets of anode half-cell samples. The first set was heat treated under forming gas and annealed for 2 h at 850 °C. The strength tests were then conducted at room temperature applying an inert Argon atmosphere. The specimens of the second set were prior to each individual test reduced with forming gas at 850 °C for 20 min while being already placed in the B3B set up. Subsequently the gas flow was upheld to maintain the reduced state during the actual testing. Thermogravimetry was used to ensure that the anode is completely reduced after 20 min, by measuring the relative mass loss of the two respective anode powders while being exposed to forming gas at the respective temperature. The displacement speed of the test rig was in general set in a way, so that fracture occurred in less than 4 s. The thicknesses of the electrodes and the electrolyte were determined optically from the edges of the cut specimens with an accuracy of ±2 μm.

2.3. Stress calculation for half-cells subjected to B3B bending

2.3.1. Half-cells with pure elastic deformation until fracture

In order to calculate the fracture stress of any layer of a multilayered elastically heterogeneous plate loaded in the B3B set up,