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Post-test analysis of an SOFC after nearly 100,000h of stack operation

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Abstract

A solid oxide fuel cell stack was operated galvanostatically for nearly 100,000h at 700°C with a current density of 0.5 A cm^{-2}. The stack consisted of two anode-supported cells with Ni/YSZ substrate, anode, 8YSZ electrolyte, GDC barrier layer and an LSCF-based cathode. The contacting was obtained with a Ni mesh at the fuel side and a perovskite material on the air side. The interconnects were made of ITM from Plansee SE, Austria. After stopping the test, all stack parts were characterized according to the internal protocols. One third of the stack was embedded and two thirds were dissected plane-by-plane.

The cell was characterized mostly by SEM on cross-sections from the stack and the individual cells. Additionally, wet chemical analysis was performed to get insight into the existence of foreign elements transported into the stack by the fuel or air. The Figure shows an overview of the microstructure of the entire cell after the test.

The results obtained so far show only little incorporation of foreign elements (Cr, Si, Al, Ca, Mg, Ti), especially when keeping the long operation time in mind. SEM characterization reveals very small inter-diffusion within the cell and the contacting, and only the cathode layer and the boundary between cathode and barrier seem to have changed. The cathode microstructure is fractionated to some extent and a second phase forms facing the GDC barrier, consisting mostly of the foreign element chromium. Further post-test analysis with higher magnification and resolution (e.g. TEM) will be performed soon. Up to now, the best statement describing the cell after 100,000 h is "relatively unspectacular".
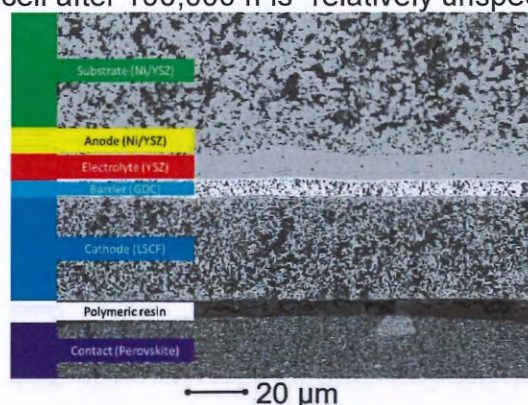
Figure: SEM cross section of the cell operated for ~ 100,000 h

Introduction

One of the critical issues in conjunction with solid oxide fuel cells is their long-term reliability. For more than 10 years, Jülich has operated numerous stacks in fuel cell and electrolysis mode for durations of more than 3,000 h. In recent years, one SOEC stack ran for approx. 20,000 h and some SOFC-stacks for 20,000 and 35,000 h [1-4]. In 2007, operation of a short-stack was started just barely before the end of the European R&D project RealSOFC [5]. This project aimed for operation times of 3,000 h to compare various materials and operation parameters. One materials-related comparison was the interconnect material used. Two similar stacks, one built with Crofer22APU and one built with ITM from Plansee were assembled and operated. The first one was shut down after 18,000 h and the latter one was operated until it reached 100,000 h at the operation temperature of 700°C. Within that time the stack was on load for 93,000 h and in the last period for 7,000 h under OCV at 700°C.

After reaching the 100,000 h, the stack was post-test analyzed according to our internal protocols [6] and all stack components characterized individually by the single experts (interconnects, sealant, cell). Here we report the results related to the cell.

1. Stack description

A 2-plane short stack of the Jülich so-called F-design was assembled with two anode-supported cells of 100x100 mm². The active area was 81 cm², the applied current density 0.5 A cm⁻², and humidified hydrogen and compressor air were used as gases. The overall voltage degradation rate reached 0.5 % per 1,000 h, but not linearly. In minimum, four different regimes / slopes could be observed [7]. After cooling down, one third of the stack was embedded completely and cut by water jet cutting from the entire stack. The other two thirds were dissected plane-by-plane. Samples from the embedded and non-embedded part were cut, ground and polished for SEM and TEM cross-sectional characterization. Other cell samples were taken for wet chemical analysis and SEM surface characterization. To compare the results obtained for the cell, a second cell from roughly the same manufacturing period as those of the stack was treated in a similar manner.

2. Results

Wet chemical analysis
Six cell samples were cut, dissolved and their chemical composition measured via ICP-OES (inductively coupled plasma – optical emission spectroscopy). Table 1 shows the results obtained.

Table 1: Wet chemical analysis of the long-term operated cell samples

Cells	Elemental amount per cm²																	
Sample								Elements										
		Zr	Y	Hf	Ce	Gd	La	Sr	Co	Fe	Ni	Mn	Cu	Si	Cr	Al	Ca	Mg	Ti
					mg cm⁻²											μg cm⁻²			
Cell 1 No. 1		120.8	21.14	2.88	2.9	1.2	8.3	2.26	1.12	2.98	209.6	0.81	232	19	517	92	12	14	67
Cell 1 No. 2		122.8	20.65	2.92	2.9	1.2	7.6	1.94	0.96	2.47	208.8	0.84	249	20	473	83	15	13	63
Cell 1 No. 3		118.9	21.15	2.79	2.9	1.2	7.8	1.97	1.09	2.67	213.7	1.2	304	38	496	105	12	12	63
Cell 2 No. 1		123.1	21.91	2.84	2.2	1.1	7.1	1.77	0.95	2.35	221.6	0.65	240	26	314	106	23	15	68
Cell 2 No. 2		123.8	21.44	2.92	2	1	8.3	2.12	1.11	2.77	218.1	0.77	287	29	423	89	21	14	69
Cell 2 No. 3		120.6	20.95	2.75	2.58	1.1	6.2	2.01	0.87	2.73	216.4	0.33	143	18	291	90	66	13	64
Layer attribution	Electrolyte+Support			Barrier			Cathode, CCL				Anode		CCL	Foreign elements					

From Table 1, we can conclude that the following foreign elements are present in the entire cell: Si, Cr, Al, Ca, Mg and Ti. Besides Cr and Al they all originate from the basic cell raw materials (proven by analyzing a reference cell). The Cr stems from the Cr species evaporation from the metallic interconnect, but the amount is relatively low for the operation time of 11 years.

<u>SEM / TEM characterization</u>
SEM characterization was performed either on samples cut from the entire stack (embedded part) or on pure cell samples from the non-embedded and dissected stack part. In Figure 1a the cathode contact layer is presented and in Figure 1b the cell's functional layers.
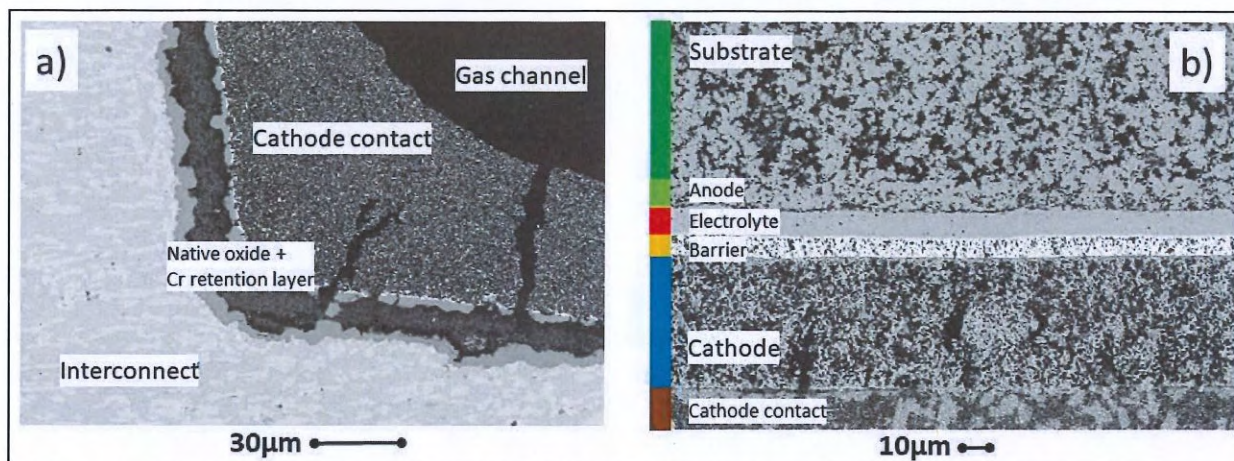

Figure 1: SEM BSE micrographs of the cells; a) cathode contact layer; b) cell functional layers.

In the cathode contact layer, EDS point analysis shows no compositional changes over the layer thickness and no incorporation of foreign elements (even no Cr). The low-magnification micrographs of the cells neither show any irregularities, nor delamination, cracks, foreign phases or obvious microstructural changes. But having a closer look at the functional layers reveals some irregularities:

- Disintegration / fragmentation of the LSCF cathode (first micrometers close to the GDC interface)
- Cr poisoning of the LSCF close to the LSCF-GDC interface
- Decoration of the GDC surface and the internal GDC pores with tiny crystals
- Elemental interdiffusion between GDC and LSCF at the interface
- Within the bulk GDC layer no foreign cell elements (neither from the LSCF nor from the YSZ)

(causing stresses and cracks). And secondly the migration of nickel toward the fuel electrode / electrolyte interface. The opposite effect, the migration away from the fuel electrode is observed in electrolysis mode frequently [1, 2, 13, 14] and happens during shorter operation times (some hundreds or thousands hours depending on operational conditions). The effect of Ni migration towards the border to the electrolyte has been theoretically postulated recently [15] but has not been observed before. We assume that the effect happens at the given operational conditions only after very long exposure times. In summary, the stack degraded with approx. 0.5 % / 1000 h but non-linearly and shows, after stack dissection, no macro failures but some microstructural effects mostly located at the border regions between the electrolyte and the first micrometers of the electrodes.

Acknowledgements

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- Up to some µm into the GDC layer diffusion of Cr
- An interdiffusion zone between GDC and YSZ; but the area is comparable to a pristine cell thus we conclude interdiffusion during sintering of the cells but not during operation (being in line with literature [8, 9])
- Foreign phase formation of a Mn and Al containing phase in the anode at the electrolyte interface (comparable to [10, 11])

All these microstructural findings can be seen in Figure 2. The elemental findings (interdiffusion, chemical EDS point analysis etc.) are not shown here. For those please refer to [12].
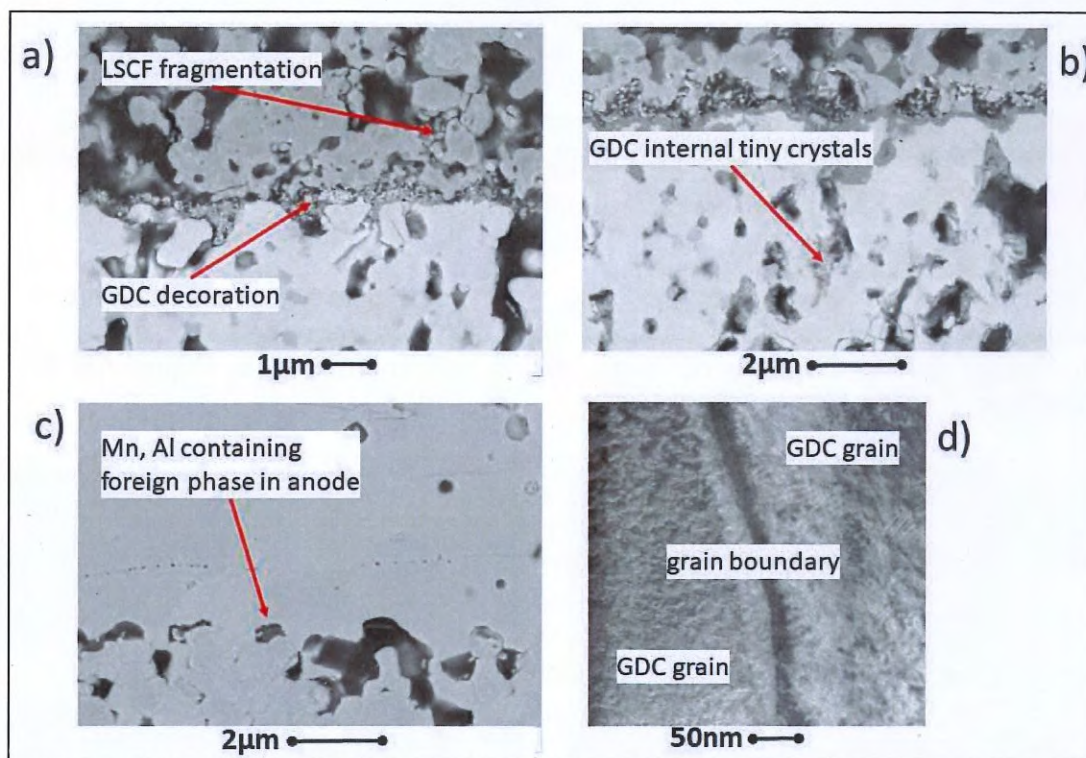

Figure 2: SEM and HAADF-TEM micrographs of the cell functional layers; a) LSCF fragmentation and GDC covering; b) internal crystal formation in GDC; c) foreign phase at electrolyte / anode border; d) TEM of two GDC grains and a grain boundary

3. Discussion

Most of the aforementioned effects can be related to the long operation time. Obviously the LSCF reacts after these long-term exposure partly with Cr species (at the interface to the ion conductor). Additionally, it seems to decompose to a certain amount. Whether the decomposition is based on the interaction with Cr or would have been happened only due to the long electrochemical operation is still unclear. What has been observed for the first time is the interaction of Cr also with the GDC barrier layer. This happens apparently only after very long times because this effect was even not observed in the stack operated for ~ 35,000 h [11]. The interdiffusion zone between YSZ and GDC shows no difference to a reference cell which means that the interaction only happens during sintering of the layers and is not ongoing during operation at 700°C.

At the fuel side two effects are interesting. Firstly, the formation of Al- and Mn-containing small foreign phases, which have been observed earlier in long term operated stacks and which cause stack failure if the size of the foreign phase reaches a certain amount