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Evaluation of the Electrical Contact Area at the SOFC Cathode

Vincent A.C. Haanappel, I.C. Vinke, L.G.J. de Haart, D. Stolten,
Forschungszentrum Jülich GmbH, Institute of Energy Research (IEF-3), D-52425 Jülich, Germany

Abstract

In the frame of the ZeuS-III project, a model study was started on evaluation the area-specific resistances (ASRs) of various layers being used in SOFC stacks. It is well known that stack performance not only depends on cell resistance but also on the electrical conductivity of the various applied contact and protective layers. Various layers have been tested under simulated SOFC conditions, and results have shown that the lowest ASR value, about 3 mΩ.cm², was obtained for an LSM (2) contact layer. A significantly higher resistance was found for the combined contact and protective layer LCC10-Mn_3O_4, being around 37 mΩ.cm². Related to the various tests, the total ASR of an F-design stack, developed by Forschungszentrum Jülich, under ideal conditions can be estimated. In this case the ASR value was calculated as the sum of that of the LCC10-Mn_3O_4 layer and the formed oxide scale due to oxidation of Crofer22APU. Contacting resistance at the anode side was considered negligible. When differences in the ASR values occurred when compared with that from current – voltage measurements performed with real SOFC stacks, this can be explained by the limited contact area between interconnect and cathode. These results can be used to model the influence of various applied layers and different geometric contact areas on the overall ASR as determined from performance measurements with SOFC stacks.

1 Introduction

The application of protective and/or contact layers on metallic interconnects in SOFC stacks is indispensable. On one hand, to inhibit chromium evaporation at the air side, and on the other, to assure good contacting between cathode and the metallic interconnect [1-3].

Poisoning of the cathode by chromium deposition is one of the main reasons of severe degradation of SOFC performance. In order to prevent chromium evaporation from the interconnect a protective layer is needed. Such a layer has to be gas tight and to possess good electrical conductivity. The use of a contact layer is needed for assuring good electrical contact between interconnect and cathode: compensation of dimensional tolerances of the parts.

Stack performance depends not only on the cell resistance itself, but also strongly on the conductivity or resistance of the various materials being used in an SOFC stack: the higher the contact resistance between the various layers and the resistance of the individual layers being applied, the lower the output performance.

This contribution deals with a model study on evaluating area-specific resistances of various individual layers as well as various combinations of layers, used as protective and/or contact layers in SOFC stacks.

2 Experimental

Each sample consists of two metallic (platinum) sheets, one sheet with dimensions of 50 x 50 mm² and the other with a size of 40 x 40 mm². In one case, Crofer22APU was chosen as the metallic sheet (50 x 50 mm²). Before applying the layer(s) to be tested both surfaces were ground with 1200 grit and rinsed with ethanol. Two Pt-wires were attached to these sheets, one for applying a current load and the other for measuring the corresponding voltage (4 point DC). An overview of the tests including the tested layers and their deposition techniques is listed in table 1. A subdivision of the series of tests is made by the purpose of the various layers, i.e. (1) current collector (LSM(1)), (2) contact (LCC10, LSM(2)) and (3) protective (Mn_3O_4) layers. Also tests with combinations of layers were performed.

Table 1: Various tests including tested layers and their application techniques.

Application	Pt – 50 x 50 mm²	Deposition technique	Pt – 40 x 40 mm²	Deposition technique
Current coll.	LSM (1)	**SP – 70 µm	-	-
Contact	LCC10	*WPS – 130-150 µm	-	-
	LSM (2)	**SP – 70 µm	-	-
Protective	Mn_3O_4	*WPS – 10 µm	-	-
Combinations	LCC10-Mn_3O_4	*WPS – 150 µm	-	-
	LCC10-Mn_3O_4	*WPS – 150 µm	LSM (1)	**SP – 70 µm
	LSM (2)	**SP – 70 µm	LSM (1)	**SP – 70 µm
	***LSM (2)	**SP – 70 µm	-	-

*WPS: wet powder spraying; **SP: screen-printing; ***Crofer22APU as the metallic sheet forming interfacial oxide layer.

All tests were run with three samples, connected in series with each other and in such mode that no differences in current load occurred between the tested samples. Figure 1 shows the three samples with Pt as the metallic sheets coated with a current collector LSM (1) layer. All samples were isolated from each other by a thin alumina plate. On top a mechanical load was applied of 5 N/cm². The furnace was heated with a rate of 2 °C/min to 850 °C. At this temperature, the samples were exposed for about 10 h, after which the operating temperature was decreased to 800 °C. This procedure simulates the heating and conditioning procedure of SOFC stacks tested at Jülich. Before the current load was applied, current – voltage measurements were performed up to 0.75 A/cm². The constant current load was set at 0.6 A/cm². After regular intervals current – voltage plots were obtained. After

500 h of exposure, the final current – voltage plot was taken followed by cooling the furnace to room temperature.

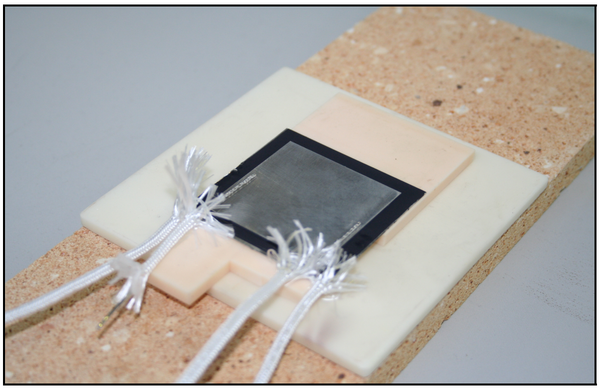

Figure 1: Left: one sample with two Pt-sheets coated with LSM (1) layer on the bottom sheet. Right: three samples "stacked" in series before testing.

3 Results and Discussion

Current collector layer: The area-specific resistances (ASRs) of three samples with Pt as the metallic sheet and an interlayer of LSM (1) being considered as the cathode current collector layer are shown in Figure 2. From this figure it can be concluded that relatively high scatter occurred between the measured ASR of the individual samples with that of sample 2 the highest and of sample 1 the lowest ASR values. Initially the ASR obviously decreased with the average value starting from about 7.7 ± 2.9 to 5.1 ± 2.6 mΩ.cm² after 500 testing hours.

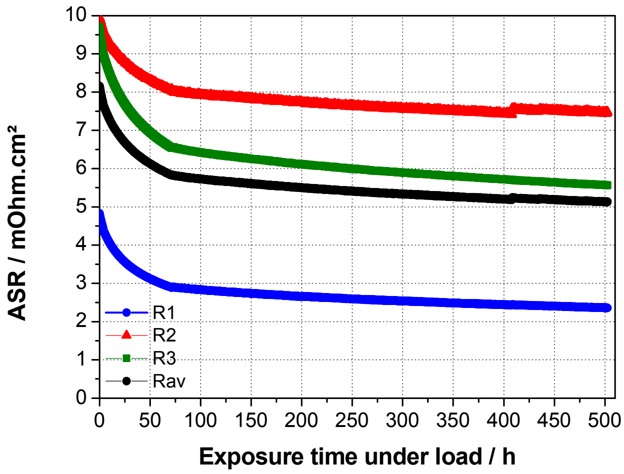

Figure 2: Area-specific resistances (ASRs) of three samples with Pt as the metallic sheets and LSM (1) as the intermediate layer being tested in air at 800 °C for 500 h. Mechanical load was set at 5 N/cm² and the applied current load at 0.6 A/cm².

The ASR values obtained after regular intervals and calculated from the current – voltage measurements are given in table 2. These values correspond well with those from Fig. 2. As such, it can be concluded that the ohmic resistance of the LSM (1) cathode current collector layer decreased with longer exposure times.

Table 2: ASR values after regular intervals of three samples with Pt as the metallic sheets and LSM (1) as the intermediate layer being tested in air at 800 °C for 500 h. Mechanical load was set at 5 N/cm² and the applied current load at 0.6 A/cm².

Specimen:	**ASR (mΩ.cm²)**						
	t = 0	t = 72	t = 167	t = 267	t = 339	t = 413	t = 504
1	4.38	2.86	2.68	2.54	2.47	2.41	2.33
2	9.62	8.05	7.78	7.62	7.62	7.55	7.46
3	9.04	6.54	6.21	5.96	5.96	5.71	5.59
Av.value:	7.7 ± 2.9	5.8 ± 2.7	5.6 ± 2.6	5.4 ± 2.6	5.4 ± 2.6	5.2 ± 2.6	5.1 ± 2.6

Contact layers: In the case of the contact layer type LCC10 with a thickness of about 140 µm, the ASR values showed an increase as a function of time, started at 36 ± 12 mΩ.cm² and ended, after 500 h of exposure at 48 ± 17 mΩ.cm². The ASR as a function of time is depicted in Fig. 3. A second type of contact layer is based on LSM (2). This layer showed similar features as those with the current collector layer LSM (1), as described before. In this case the average value of the ASR was about 4.6 ± 2.2 mΩ.cm² at the beginning and 3.3 ± 1.6 mΩ.cm² after about 500 h of testing.

Based on only the ohmic resistance, it would be recommended to use this type of contact layer. However, nothing can be concluded about the effectiveness of such a layer, in particular about mitigating or preventing chromium evaporation from the interlaying interconnect and thus avoiding chromium poisoning of the cathode.

Protective layer: The tickness of the protective Mn_3O_4 layer applied by wet powder spraying was only 10 µm. The measured ASR was initially about 24 ± 6 mΩ.cm² and decreased to about 17 ± 5 mΩ.cm², this as a result of densification and improved contacting between the individual grains during sintering at 800 °C.

An overview of the ASR values for the current collector, the contact and the protective layers are given in table 3. All values are average values of three samples measured simultaneously.

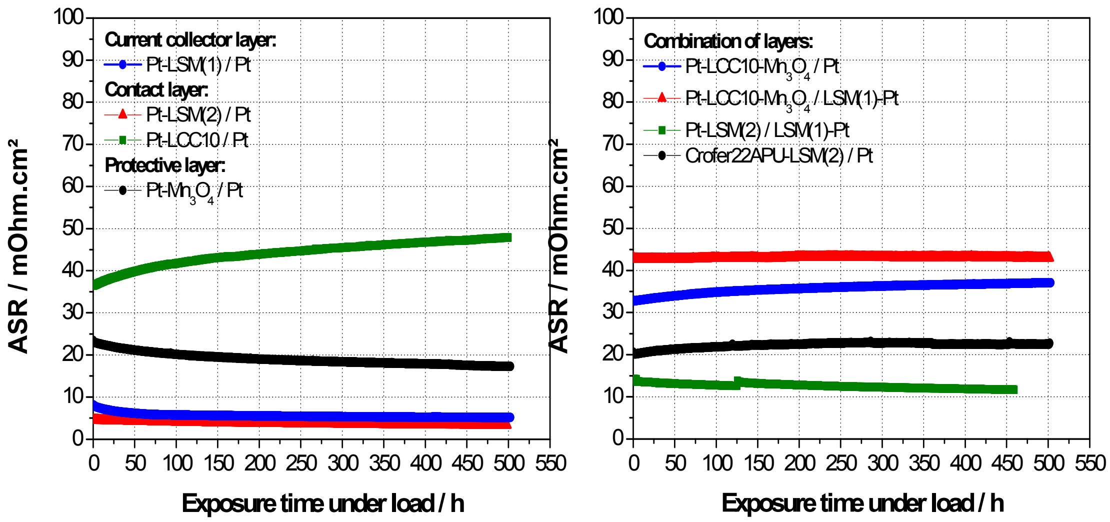

Figure 3: Area-specific resistances of samples with (left) current collector layer LSM(1); contact layers LSM(2) and LCC10; or protective layer Mn_3O_4 as the intermediate layer, (right) combinations of layers tested in air at 800 °C for 500 h. Mechanical load was set at 5 N/cm² and the applied current load at 0.6 A/cm². All curves are average values of three samples measured simultaneously.

Table 3: ASR values (mΩ.cm²) of various layers with Pt as the metallic sheets being tested in air at 800 °C for 500 h. Mechanical load was set at 5 N/cm² and the applied current load at 0.6 A/cm².

	Current collector	Contact		Protective
	LSM(1)	LCC10	LSM(2)	Mn_3O_4
t = 0 h	7.7 ± 2.9	36 ± 12	4.6 ± 2.2	24 ± 6
t = 500 h	5.1 ± 2.6	48 ± 17	3.3 ± 1.6	17 ± 5

Combination of layers: Experiments were also performed with a combination of protective and contact layer LCC10-Mn_3O_4, which is used in the Jülich-type SOFC stacks [4]. Results from the endurance tests are shown in Fig. 3 (right) depicting the ASR as a function of the testing period. The calculated ASR values from the current – voltage measurements at t = 0 and t = end are given in table 4. Based on these results, it can be concluded that the ASR slightly increased from 33 ± 10 to 37 ± 13 mΩ.cm² during exposure in air at 800 °C. The total of the individual ASR values for both layers is at t = 0 about 60 and increased slightly up to about 65 mΩ.cm², thus somewhat higher than that of those values obtained with the double layer LCC10-Mn_3O_4.

The increase of the ASR over the total exposure time was for both similar, but the absolute differences in the ASR values can be explained by differences in contacting area between the separated layers, small differences in thickness of the individual layers, or the formation of a high conductive interlayer between both layers, improving the overall conductivity of the samples.

Another combined testing was that with applying on one sheet LCC10-Mn_3O_4 and on the other LSM (1) contact current collector layer. The area-specific resistance was during the whole exposing time around 43 ± 7 mΩ.cm². The recorded ASR values for the three samples are shown in Fig. 3(right). Sum of the ASR values for the individual tested layers, measured separately, was at the beginning about 39 ± 7 mΩ.cm² and after 500 h of exposure slightly increased to values around 42 ± 8 mΩ.cm², thus with good comparison.

A combined experiment was also performed with the contact LSM (2) layer and the current collector LSM (1) layer. The ASR values as a function of the exposure time are shown in Fig. 3(right). At t = 0, the ASR value was 14.3 ± 1.2 mΩ.cm² and after about 500 h 11.7 ± 2.0 mΩ.cm². The total ASR of the individual layers, determined separately, was at the beginning 12.4 ± 2.5 and after 500h testing 8.4 ± 2.1 mΩ.cm². This means that the decrease and the sum of the ASR values of the individual tested layers are comparable with those obtained with the testing of the double layer.

Next to the contribution of the individual layers, i.e. LCC10, Mn_3O_4 and LSM (1) cathode current collector layer, the total ohmic resistance of an SOFC stack and the influence of the interconnect alloy Crofer22APU on the ohmic resistance has to be evaluated, as well.

The underlying experiment is based on the use of Crofer22APU as the metallic sheet with on one side the LSM (2) contact layer. The opposite sheet is uncoated Pt. Results from the test are summarized in Fig. 3(right). The ASR value slightly increased from 22.4 ± 6.9 to 22.9 ± 5.5 Ωm.cm² after 500 h of exposure.

Table 4: ASR values (mΩ.cm²) of various layers with Pt or Crofer22APU as the metallic sheets being tested in air at 800 °C for 500 h. Mechanical load was set at 5 N/cm² and the applied current load at 0.6 A/cm².

	Combination of layers			
	Pt – LCC10-Mn_3O_4 / Pt	Pt – LCC10-Mn_3O_4 / LSM(1) - Pt	Pt – LSM(2) / LSM(1) - Pt	Crofer22APU – LSM(2) / Pt
t = 0 h	7.7 ± 2.9	36 ± 12	4.6 ± 2.2	22.4 ± 6.9
t = 500 h	5.1 ± 2.6	48 ± 17	3.3 ± 1.6	22.9 ± 5.5

In comparison with data obtained from tests with two Pt sheets and an LSM (2) contact layer, it is clear that the calculated ASR with Crofer22APU as the metallic sheet is obviously higher, i.e. 22.9 ± 5.5 mΩ.cm². In the case of the former, the ASR decreased from 4.6 ± 2.2 to 3.3 ± 1.6 mΩ.cm². The higher ASR can be explained by the use of Crofer22APU forming a small interfacial oxide layer with relatively low conductivity. Earlier measurements revealed [5] that the ASR of Crofer22APU oxidized for 300 h at 800 °C was between 10 and 30 mΩ.cm², which corresponds well with the measurements presented here. The oxide scale, formed during the exposure period consists of an inner chromia and an outer manganese-chromium spinel layer and is thus responsible for the higher measured resistance. Taken into consideration also the ASR values measured during single cell testing with anode-supported SOFCs with LSM- or LSCF cathode, some conclusions can be drawn concerning the contribution of the various applied layers including interconnect material to the overall ASR as determined from stack measurements. Table 5 shows the ASR values for both types of single cells, tested at Jülich [6].

Table 5: Area-specific resistances of anode-supported SOFCs with LSM or LSCF cathode as function of the operating temperature [6].

Temperature (°C)	SOFC with LSM Cathode	SOFC with LSCF cathode
	ASR (mΩ.cm²)	ASR (mΩ.cm²)
800	190 ± 6	120 ± 6
750	260 ± 11	140 ± 6
700	430 ± 10	170 ± 4

From this table it can be concluded that the ASRs of both types of SOFCs increased with lowering the operating temperature. In the case of SOFCs with LSM cathode, the calculated ASR (800 °C; 700 mV) from current – voltage measurements under standard conditions is about 190 mΩ.cm². As an example, these data can be compared with that of an SOFC stack including SOFCs with LSM cathode [4]. Such a stack is constructed of Crofer22APU (cell frames and interconnect).

Contacting the cathode with the adjacent interconnect was achieved by Mn_3O_4 LCC10 layers applied by wet powder spraying. Based on the ASR data, the following conclusion can be drawn. A rough estimation of the total ideal ASR in first approach is assumed to be the sum of the $ASR_{SOFC\text{-}LSM}$, the $ASR_{LCC10\text{-}Mn3O4}$, and the $ASR_{Crofer22APU}$: 190 + 40 + 20 = 250 mΩ.cm² (more tests are planned to verify the results in more detail). Contacting resistance on the anode side (Ni-Ni) was here neglected. In the case of an SOFC stack the ASR on average is 260 mΩ.cm² [4], which corresponds well with the sum of the individual tested layers, presented in this contribution.

Based on the geometrical factor because of the limited contact area in an SOFC stack, a larger difference was however expected. The underlying measurements showed that this additional loss was negligible or at least relatively small indicating that this contribution plays only a minor role of importance. The contribution of the formed oxide scale between the metallic interconnect and the applied protective layer is in this case more obvious.

4 Conclusions

With a simple test method the area-specific resistance of various layers was evaluated individually. Contact layers are being used in SOFC stacks aiming improved contacting between the cathode of solid oxide fuel cells and the metallic interconnect. Three specimens with various types of layers could be uniformly loaded by a constant current load.

Resistance measurements have shown that in the case of simulating SOFC stack conditions, the lowest ASR was measured for the LSM (2) contact layer. In the case of the F-design JÜLICH stack, the total ASR was calculated by the sum of that of the contact and protective layer LCC10-Mn_3O_4 and the formed oxide scale. The difference between this calculated ASR and that obtained from current – voltage measurements with a real SOFC stack was almost negligible. As a consequence, the limited contact area between the interconnect and the cathode plays only a minor role of importance.

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