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ENHANCING THE LIFETIME OF SOFC STACKS FOR COMBINED HEAT AND POWER APPLICATIONS

SOF-CH

Rapport annuel, EPFL-LENI, 2007 : WP 2 CATHODE

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RESUME

In this first year of thesis work, literature has been reviewed and the usual experimental techniques introduced (cathode paste preparation, screen printing, sintering, single cell assembly, impedance spectroscopy, electron microscopy). A number of different cathode mixtures (usually 50-50 vol% of LSM and 8YSZ) has been tested in small sized single cells (1 cm^2 active area, metal mesh current collection), generally giving adequate performance (>0.8 V @ 0.5 A/cm^2, and ca. 1 A/cm^2 @ 0.7 V, 800°C). These tests allowed the following observations : the nature of current collection is important (LSC instead of LSM, 0.7 V vs. 0.6 V for 1 A/cm^2), the zirconia origin and proportion is important (8YSZ from MEL (UK) giving better output than 8YSZ from Tosoh, 1.2 A/cm^2 vs. 1 A/cm^2 @ 0.7 V), replacing 8YSZ by 10ScSZ, however, brought only a small improvement, where it is to be questioned whether this justifies the use of more expensive ScSZ, even when used in small quantities. The regular cathode to date showed -28 μV/h decay (ca. 4%) over 1000 h (800°C) at 1 A/cm^2 in one longer termed test (1400 h). Best performance to date was obtained by using powders of high surface area (both for LSM in the composite cathode and for LSC as current collector), reflected in low ohmic drop (0.07 Ωcm^2 vs. typically >0.1 Ωcm^2), voltage loss attaining -9 μV/h @ 0.5 A/cm^2 (800°C) for the last 2000 h of a 4000 h run (ca. -0.9%/1000h). Post mortem analysis of most tests is still required.

A systematic test series has been carried out for fixed durations, of 5 identical cells (0, 24, 72, 200 and 1000 h) polarised under identical conditions (850°C, 0.6 A/cm^2). Their microstructures will be determined quantitatively using SEM and an imaging technique. It will be attempted to link these results to electrochemical modelling efforts, that have been started with the help of Prof. P. Costamagna (Univ. Genoa, IT).

Reaction couple tests (LSM-YSZ, LSM-ScSZ, LSM-GDC, 850°C, 1500 h) are ongoing. A sealed single cell test rig has been constructed and validated; other test rig options are under evaluation. A multi-cathode test rig has been taken in operation allowing to simultaneously characterise 4 cathodes (with individual galvanostatic control) for parameter variation and optimisation.

Goals

The goal is to understand the degradation of LSM-YSZ type SOFC composite cathode and to optimise its microstructure to limit this degradation.

Performed work and obtained results

Literature

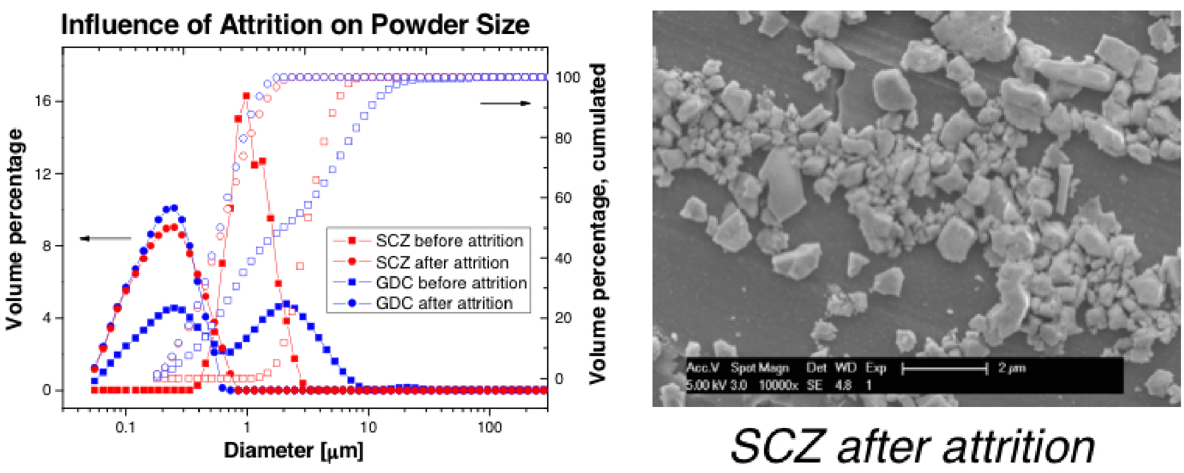
A bibliographic study was carried out. One of the main drivers of the work is the electrochemical composite model developed by Prof. P. Costamagna, Univ. Genoa (IT), who also acts as external coach for Pietro Tanasini's thesis. It reveals in particular optimal performance for a 45%-55% (vol) ratio of LSM-YSZ (using 0.3 μm spherical monosized particles); the promising model still lacks clear experimental validation, which the present work aims to deliver.

The International Workshop on Fuel Cell Degradation held in Creta (Sep 2007) allowed to update the present knowledge also for cathode durability. Operation at high current density and especially high overpotential tends to degrade LSM cathodes fast, because of non-conducting $La_2Zr_2O_7$ (LZR) formation, leading to the peculiar behaviour (confirmed experimentally also at EPFL) that such cathodes are more durable at higher temperature (850°C vs. 750°C) since they then show smaller overpotential loss. The low thermal expansion coefficient of LZR (7) compared to that of YSZ (10.7) and LSM (11.8) in addition causes delamination of LSM particles from the YSZ structure. Recommended practice is thence to operate at high cell voltage (>0.7, or better >0.8 V). The mechanism of Cr-poisoning (from metal interconnects) with LSM cathodes is that of $CrMn_2O_4$ spinel formation at the triple phase boundary. Other impurities (Si, Na,..) even in very small quantities may have large effects on stability. Another degradation effect is that of elemental redistribution in LSM related to local PO_2 conditions; again small thermodynamic shifts may lead to large stability variations. According to Risø National Laboratory (DK), the cathode did not degrade in pure O_2 (unlike in air) even at current density as high as 1.2 A/cm^2. The LSM limiting step is believed to be slow incorporation of adsorbed oxygen species.

Materials

<u>Powders</u>

$(La_{0.75}Sr_{0.25})_{0.9}MnO_3$ was obtained from Praxair via HTceramix, and electrolyte powders from HTceramix (8YSZ Tosoh) and SOFCpower (10YSZ, 10Sc1CeYZ, 20GDC). The latter 3 powders have been attrited to reduce average particle size to 0.25 μm (Fig. 1) and were thoroughly characterised (H. Lübbe, Laboratory of Powder Technology, EPFL). They will be used in cathode composites later on – for the time being standard mixtures with 8YSZ have been tested.



<u>Fig. 1</u> : Particle size distribution before and after attrition of ScSZ and GDC; d_{90} is below 400 nm for both powders (courtesy Henning Lübbe – EPFL-LENI & EPFL- LTP).

Paste

For screen printing paste preparation, a triple roll mill is used for adequate homogeneisation. The paste rheology is being properly characterized at EPFL-IMX (viscosimetry) for reproducibility.

Reaction couples

Three mixtures of LSM powder with the electrolyte powders (10YSZ, 10ScSZ, 20GDC) have been pelletized and are soaked at 850°C in air since 1200 h. Treatment will continue until reaching 1500 h. The reaction couples will then be XRD- analyzed (EPFL – LC) and TEM analysed (EMPA).

Instrumentation

Test rig(s)

A new sealed test rig based on quarz tubing has been taken in operation (Fig. 2). A first symmetrical cell (Pt/0.4 mm YSZ support/Pt) has been mounted (gold ring seals) and tested, theoretical OCV was obtained.

Several alternative rigs for testing (symmetrical cells, full cells) will be taken in operation over the next months (with particular attention to avoid influence from Cr poisoning originating from setup metal parts) :

- a sealed cell-on-alumina tube test rig will be purchased from SOFCpower (Italy) - delivery Jan 2008
- a sealed alumina tube test rig (Probostat™) is on order from Norway – delivery Dec 2007
- our current sealless metal flange test rigs (advantageous in the sense that constant pressure is exerted on the current collectors, to avoid contact losses during long term measurement) are being improved (Inconel 602 instead of 600; ceramic coating)

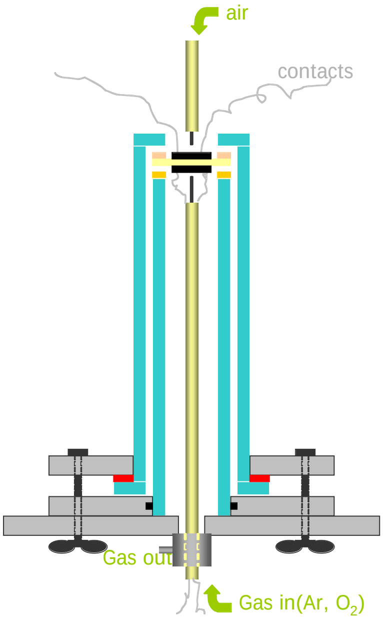
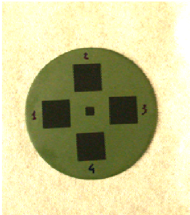


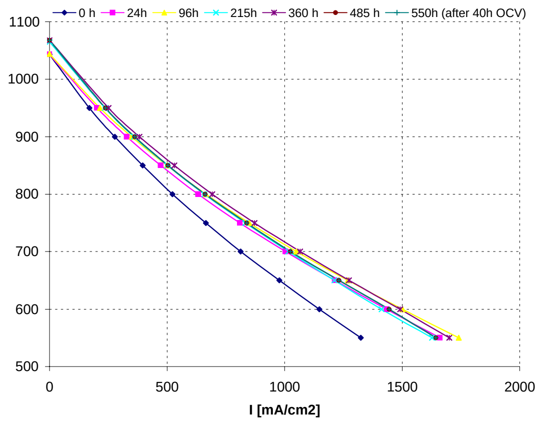
Fig. 2 : Quarz-tube, gold sealed SOFC test rig

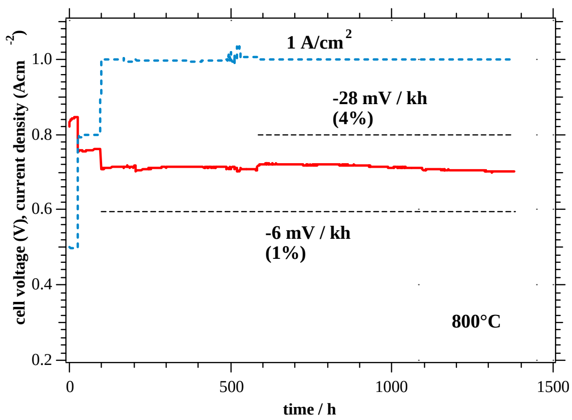


A multi-channel (4) galvanostat has been designed at EPFL–LEI and assembled at EPFL-LENI. It allows simultaneous operation of 4 cathodes (1 cm^2) on the same anode support half cell, with individual control of current density on each cathode. This bears the great advantages of a gain in test time and of direct comparability of 4 cathodes, since test conditions are rigourously identical (anode, temperature, gas flows).

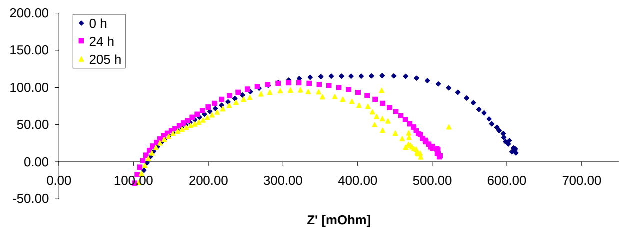
Electrochemical Results

1. LSM-8YSZ 50-50 (vol%), 32 μm thick, 1100°C, CCC=LSC, 1400 h (test EC54)



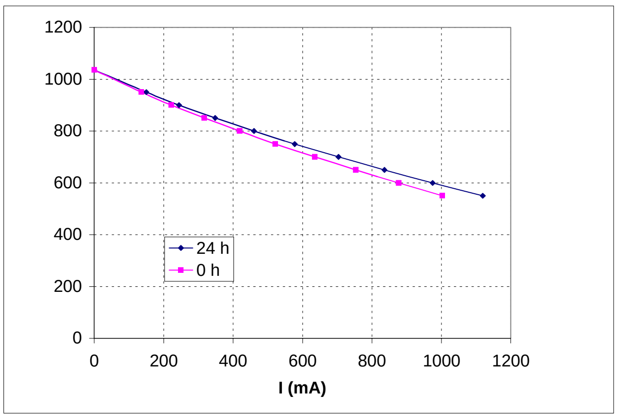


High performance was obtained, with 1 A/cm^2 at 0.7 V and 800°C, and reasonable stability of -6μV/h for the test duration (but -28μV/h over the last 800 h). The impedance spectrum shows regular ohmic drop (0.11 Ωcm^2) and low polarisation loss even at OCV (0.4 Ωcm^2). Current collection was achieved with an unsintered $La_{0.5}Sr_{0.5}CoO_3$ slurry.



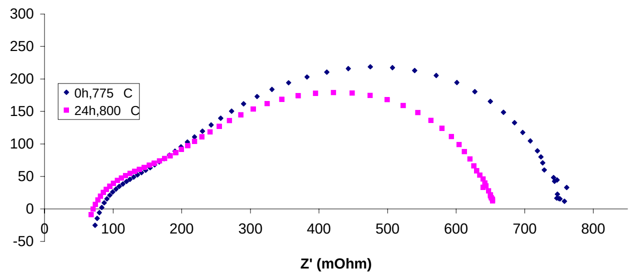
2. LSM-8YSZ 50-50 (vol%), 29 μm thick, 1100°C, **CCC=LSM**, 200 h (test EC55)

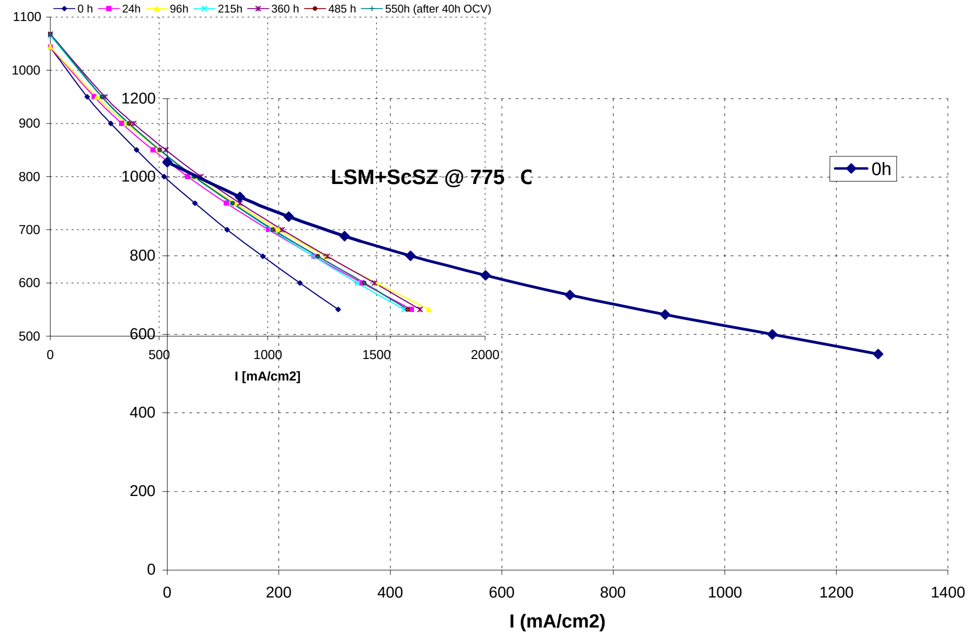
The same cathode as under (1) was now contacted with a pure LSM slurry sintered at 1000°C : a considerable performance drop can be noticed (1 A/cm^2 at 0.6 V, or 0.7 A/cm^2 at 0.7 V). This indicates the importance of cathode current collection (CCC), where LSC gave consistently the best results in all comparative tests; however, due to its intrinsic instability and reactivity, an alternative CCC has to be found. Test was carried out over 200h with a small decay.



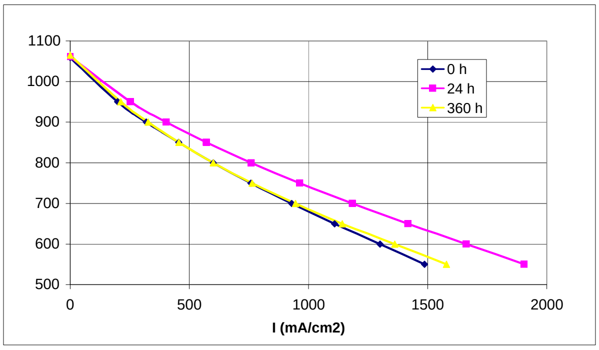
3. LSM-**10ScYSZ** 50-50 (vol%), 13 μm thick, 1100°C,CCC=LSC, 100h (test EC57)

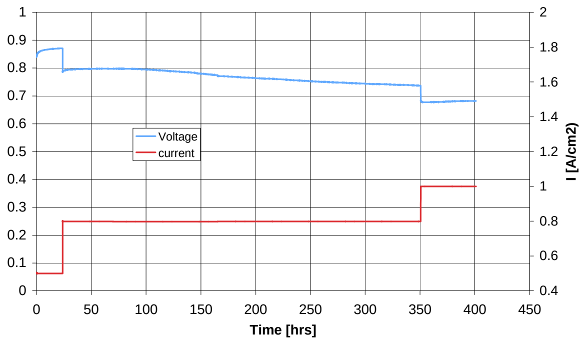
Replacement of YSZ by ScSZ (Seimi) in the composite caused a small performance increase (0.85 V @ 0.5 A/cm^2, 0.775 V @ 0.8 A/cm^2, 800°C), mainly because of lower ohmic drop (80 $m\Omega cm^2$). Stable for the test duration of 100h. Higher price of ScSZ compared to YSZ, even though used in only small quantities, has to be considered for this small improvement.





4. LSM-8YSZ 50-50 (vol%), 28 µm thick, 1100°C, CCC=LSC, 450 h (test EC57)

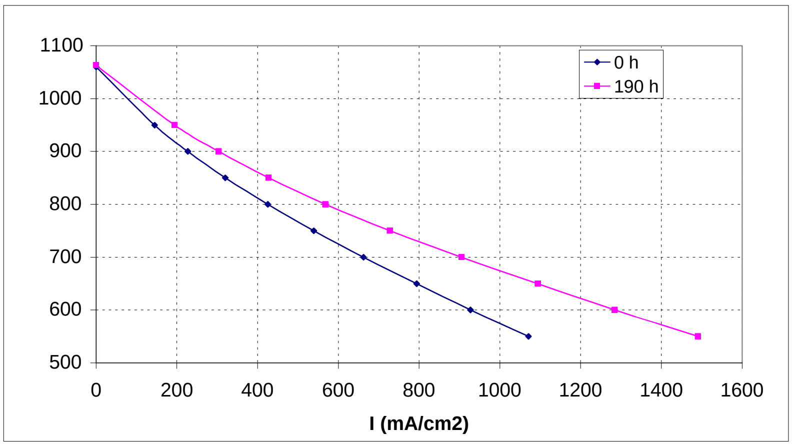




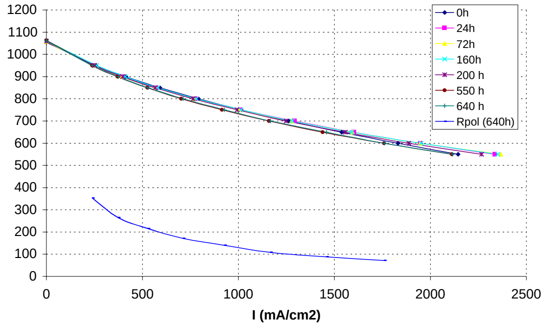
Here 8YSZ from Tosoh was replaced by 8YSZ from MEL (Magnesium Elektron, UK); also the paste preparation was modified. Highest initial performance was registered (1.2 A/cm^2 at 0.7 V, 800°C). Ohmic drop was 0.1 Ωcm^2. However, constant polarisation at 0.8 A/cm^2, unlike test 1, induced voltage decay.

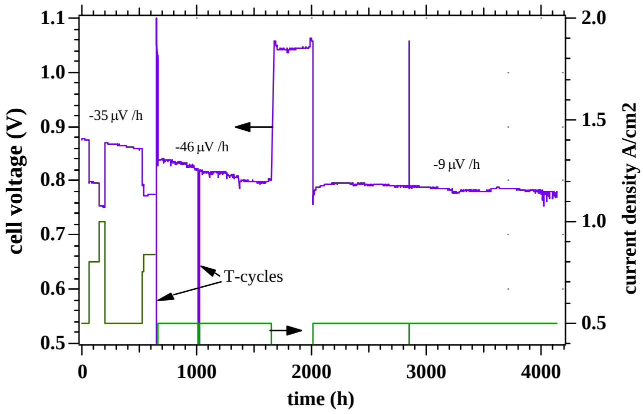
5. LSM-8YSZ **57-43** (vol%), 22 µm thick, 1100°C, CCC=LSC, 250 h (test EC58)

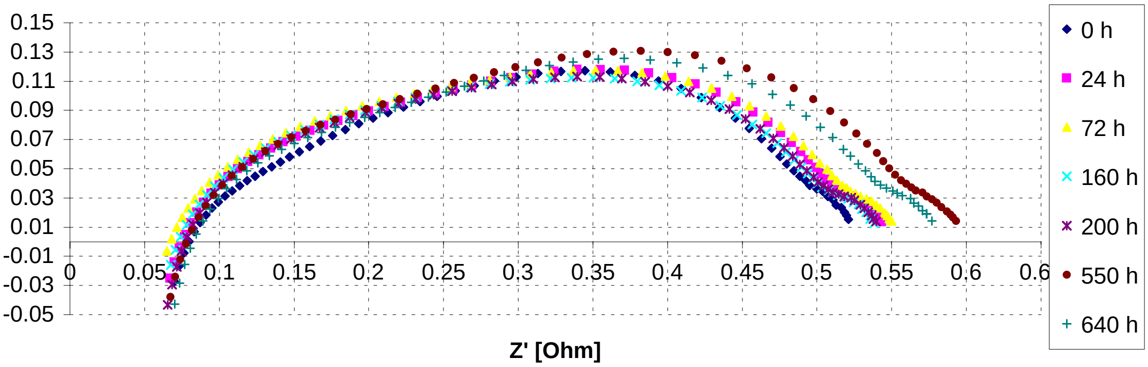
As the 8YSZ from MEL was slightly coarser than 8YSZ from Tosoh, an attempt was made to increase the LSM amount in the composite : however, clearly performance was worse than for the 50-50 mixture (0.95 A/cm^2 @ 0.7 V, 800°C). For the short duration of 250 h at 0.5 A/cm^2, performance was stable.



6. LSM-8YSZ 50-50 (vol%), 23 μm thick, 1100°C, CCC=LSC, 4150 h (test EC60)





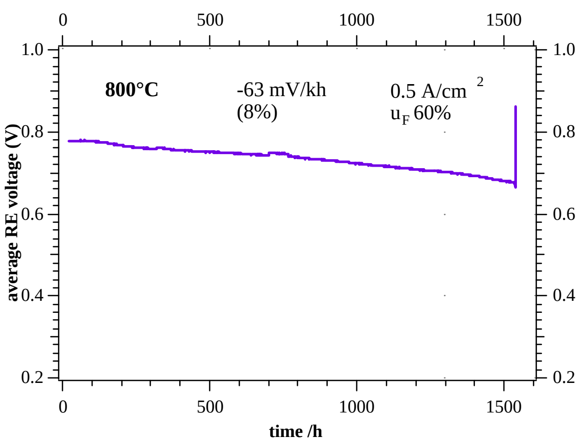


This particular test combined all best options available to present knowledge. Very high surface area powders of LSM and LSC were used (academic supplier); LSM was mixed in 50-50 vol% ratio with 8YSZ from MEL using the standard paste procedure (terpineol-ethylcellulose). Two thermal cycles were operated after 600 h and 1000 h due to furnace occupation. Highest performance of 1.3 A/cm^2 @ 0.7 V and lowest ohmic drop of 0.07 Ωcm^2 was obtained. At 0.5 A/cm^2, decay was only -9 μV/h for the final 2000 h, which is still -0.9%/1000 h.

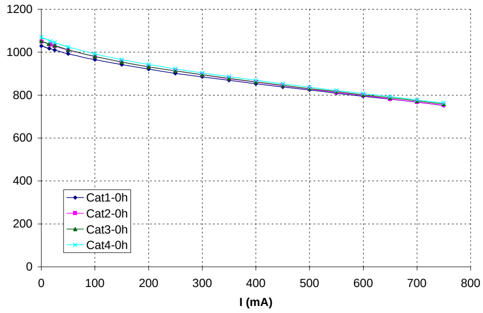
It is obvious that all samples require post test analysis in order to try and explain these differences in behaviour.

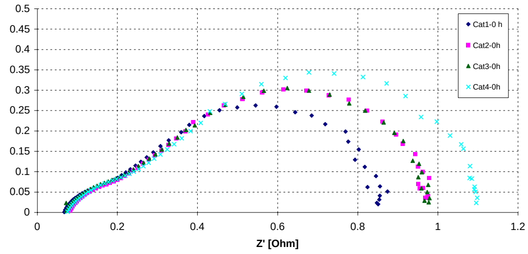
7. LSM-YSZ cathode in five-cell stack

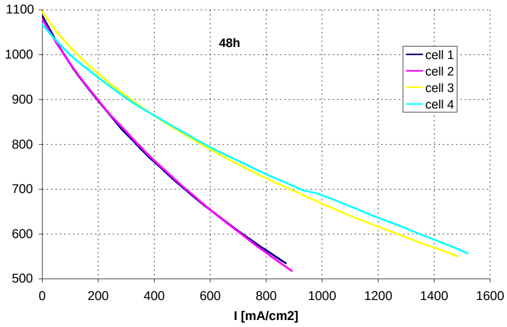
The standard HTceramix cathode (LSM-YSZ, 50-50, MEL, 1100°C, LSC CCC) was transfered to stacks (50 cm^2 active area cells) and operated at 800°C under constant load (0.5 A/cm^2, 60% fuel utilisation). Good performance was confirmed (initial repeat element voltage of 0.78 V, to be compared with 0.85 V cell voltage for small single cell tests), but decay important with -63 μV/h. This value, however, includes degradation on contacts, interconnect (without protective layer) and anode as well.

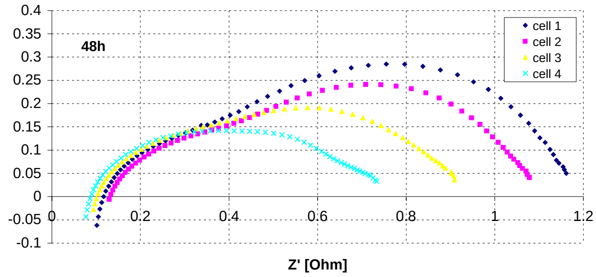


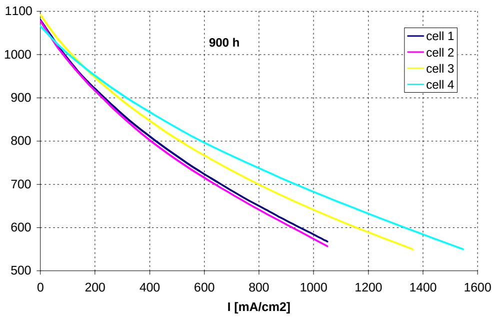
Multi-cathode operation

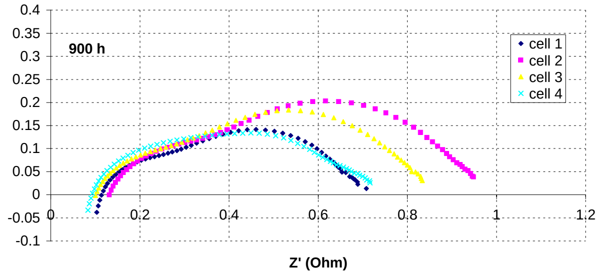






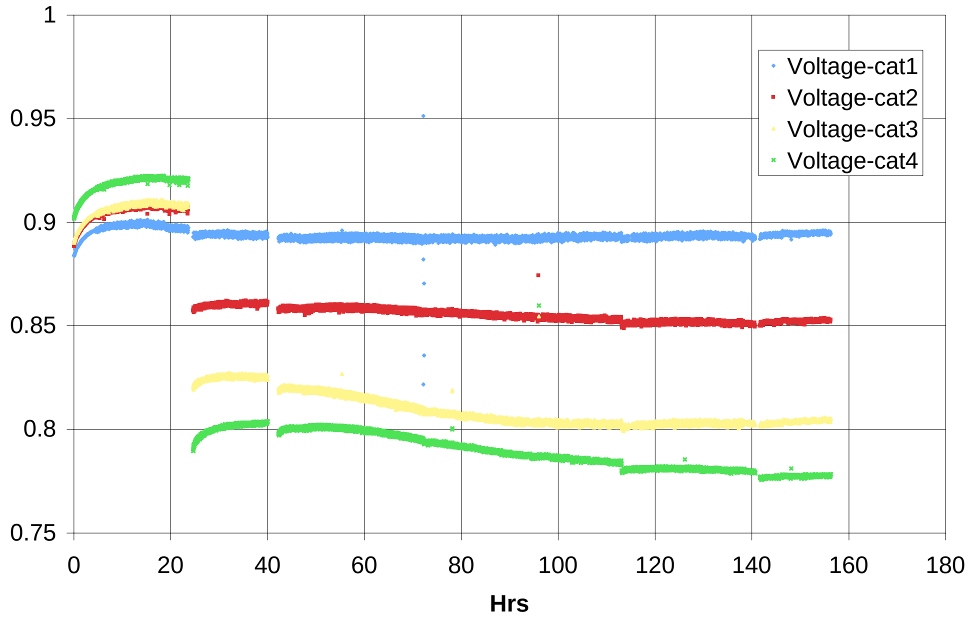






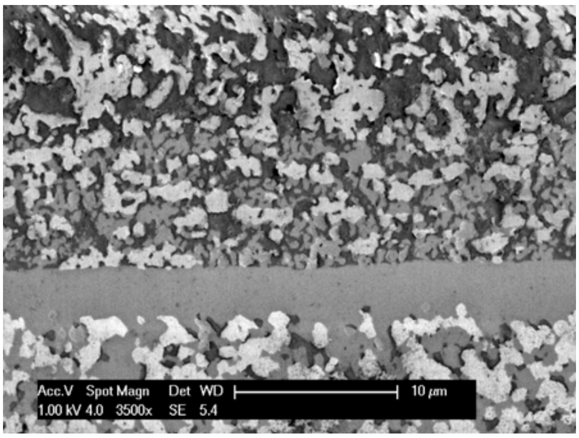
The multi-cathode test rig was first validated by operating 4 identical cathodes under identical conditions (top left and right graphs). In a subsequent step (4 lower graphs, at beginning and end of test), the cathode slurry preparation method was varied (50-50 vol% LSM and 8YSZ Tosoh) : cathodes 1 and 2 were prepared from individual dispersions for LSM and YSZ, whereas cathodes 3 and 4 were made by dispersing both powders together, using a different solvent for cathode 3 (terpineol) and 4. Clearly the codispersed powders yield better performance.

In a next test, current density was varied to assess cathode stability as a function of this parameter, all other cell conditions (anode, temperature, gas flows) remaining constant. Results are plotted on the next figure for polarisation at 850°C and current density at 0.3 (blue), 0.45 (red), 0.6 (yellow) and 0.75 A/cm^2 (green). The test has been repeated for a 900 h run followed by a thermal cycle. Data will be supplied in a next report.



Cathode series for microstructural analyses

A series of identical standard cathodes (1 cm^2) was prepared (always on HTceramix anode supports) for operation of chosen durations (0h, 24 h, 72 h, 200 h, 1000 h) at 850°C and 0.6 A/cm^2. After these fixed polarisation durations, the test was interrupted to recover the cell. The motivation is to quantitatively analyse the microstructure of these cathodes by SEM and image analysis, to try and check whether microstructural changes occur that could explain the initial performance activation (typically first 24 h) and the onset of degradation. All electrochemical tests have been performed and samples await SEM analysis. A. Faes of EPFL-LENI and EPFL-CIME has developed a quantitative image analysis tool for the SOFC anode, which can probably be applied to the cathode composite as well. The SEM graph below shows a clear contrast picture allowing to separate LSM (clear) from YSZ (grey) and pores (dark).



National collaboration

Within *EPFL*, close collaboration is engaged with the Group of Electrochemical Engineering (*GGEC*, Prof. Comninellis) who is hosting P. Tanasini for his thesis work; with the Interdisciplinary Centre of Electron Micrcoscopy (*CIME*, Dr A. Hessler-Wyser, A. Faes) for microstructural analysis, and with the Laboratory for Powder Technology (*LTP*, Prof. Hofmann, H. Lübbe) for characterisation techniques.

Strong interaction with other Swiss partners (*Empa-HLK*, *Hexis*, *HTceramix*) through the projects ***SOF-CH*** (*SFOE*, swiss*electric* research) and ***Woodgas-SOFC*** has been reported last year.

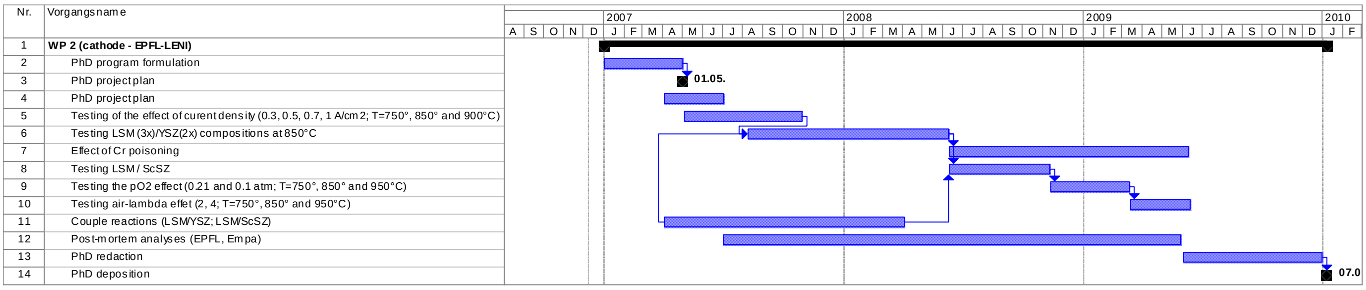
International collaboration

Coaching of P. Tanasini's thesis has been obtained from the *University of Genoa* (Italy) by Prof. Paola Costamagna. *Risø National Laboratory* (Denmark) is currently hosting P. Tanasini for a 2-month student internship (Oct-Nov 2007); the topic of investigation is the influence of humidity (0-20% steam) on the performance and durability of the LSM-YSZ cathode. Other interactions have taken place through visiting scientists active in cathode research at *EPFL-GGEC* and *EPFL-LENI*, Dr Cécile Lalanne from *CNRS Bordeaux* (F) on nickelate cathodes, Dr Lars Hildebrandt from *KTH Stockholm* (nickelates) and Dr Cristina Saez Jiminez (*University of Madrid*, LSM-YSZ), who each stayed for periods of 3-4 months at *EPFL* during 2007.

Evaluation 2007 and perspectives 2008

This one-year *SFOE* kick-off project has given an excellent start to the PhD thesis work on cathodes. Literature has been reviewed, training with the usual techniques has been given and first systematic studies initiated.

In the follow-up work in 2008, carried out within the *swisselectric research* project, quantification of the cathode microstructure will be undertaken, the paste rheology finalised, the sealed cell test bench mounted at *EPFL-GGEC*, and electrochemical modeling implemented with Prof. Costamagna. Test series as defined in the submitted proposal, as part of the thesis plan, will be carried out.



The current version of the thesis plan is given in the following (a worked version will be presented in 2008 to the doctoral school of *EPFL*).