

# Application note S-AN-01

## “Reduction process for coin cells”



MaterialsMates Italia

## Intro

during the different installations of the gas delivery system, our company executed quite a large number of SOFC experiments, mainly starting procedures, that were usually performed to validate the system.

Is a common request to know from us more on what we usually do, to be used or just to be compared with the startup procedure in use in the lab, so we decided to issue this short application note on the SOFC reduction process.

The process we describe is a sort of “merging” of different experiences coming from the user or from daily work, and is representing a reasonable way of proceeding, with some tips that can be useful

**WARNING** these informations are supposed to be correct and are coming from field experience: in no sense the given information can substitute the indication given by the samples' producers or testing labs, neither can constitute a guarantee of the performance of the samples and/or the system itself.

The information is given on a “as is” basis, and the updating of it to a more high knowledge level is not mandatory for us.

The paper contains informations widely known and considered “public”, no specific expertise was presented neither patented intellectual property.

The reader declare to understand and accept this “no responsibility” statement.

## THE CELL AT THE START

most of our plants have a SOFC cell of the “gold seal” type, where a ring made of pure gold acts as a gasket for the separation of the anodic and cathodic chambers.

This rings, usually obtained from a round wire, is placed under the sample and need to reach temperatures of about 900 C° to soften enough to form the tight seal requested. For this reason we cannot assume the two gas are well separated up to the moment the seal start to work (later on this chapter the detection of this status).

The gas composition is then affected, during the temperature ramp up , by the possibility of the air (or oxygen) to oxydize the anode electrode and the need to counteract it.

The user must decide if is more dangerous for the anode to receive oxygen or for the cathode see the hydrogen: in both cases some water will be produced where the two gases mix together, but it can be decided if this happens in the anodic or in the cathodic side as described later.

## GAS FLOWS THEORY AND PRACTICE

the first thing considered is the quantity of gas needed for the experiment in terms of mass flow, and the theory obviously refers a stochiometric ratio of the anodic and cathodic side flows in order to have the oxygen availability matching the hydrogen on the other side.

Working with air vs H<sub>2</sub> 100% give a flow ratio of 2,38 to 1 in volume/time to match 2 H<sub>2</sub> for each O<sub>2</sub> .

Then we can consider what is the amount of gas for a given current out and , just to give an example, a one inch cell with 17 mm dia electrodes must run at full load with 32 and 76 ml/ min on the anodic and cathodic side respectively.

This size of cell is the one we refer during all this part, so remember to scale if needed.

These theoretical values have to be avoided for two good reasons.

The first is the consideration of the losses due to gas leaks around, that can burn out the gas thus keeping the process limited by chemical availability.

Is true that these leaks are to be avoided, so in theory they have to play a minor role, let's say no more than 20% worst case, but nobody can easily measure them.

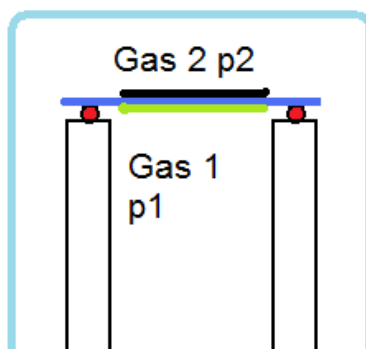
The second is that, with an usage near 100% of the fuel, the gas path and the real, uniform access of fresh gas to the surface became extremely important, but an accurate gas flow study is extremely difficult in such tiny samples.

Due to the fact the target of such equipment is to study the materials, and not the cell's efficiency, is a good rule to overflow the sample's surfaces with plenty of gas: on the one inch cell we mentioned before a healthy 200 mL/min or more on hydrogen side is not uncommon.

The reason to leave the stoichiometric ratio is a little bit more complicated and comes from the consideration of the real case of a gold ring.

Assume we have a real seal, tight enough to give us a good OCV (above 1 V at 850 C°) but not good enough to come close to theoretical value.

The section of the sample mounting is as depicted here (we have avoided to draw the electrodes for simplicity):



the red circles are the sections of the gold ring and across it there is a leakage. In order to minimize this cross flow the ideal situation is to have  $p_1 = p_2$  so, nulling the differential pressure, the diffusive process is the only reason responsible for the migration. If the two gas path in the cell (anodic and cathodic) are roughly the same, the pressure there is function mainly of the flow ratio.

So, using two equal flows give us a better chance to minimize it.

Now we can face the start of a SOFC sample passing through the different steps: temperature rise, conditioning, reduction, stabilisation, use and load run.

### Temperature rise:

the ramp rate must be between 2 to 6 C° minute to avoid the stress on the sample that can lead to a damage of electrode/electrolyte interface: as a general rule, the thicker the sample the lower the rise.

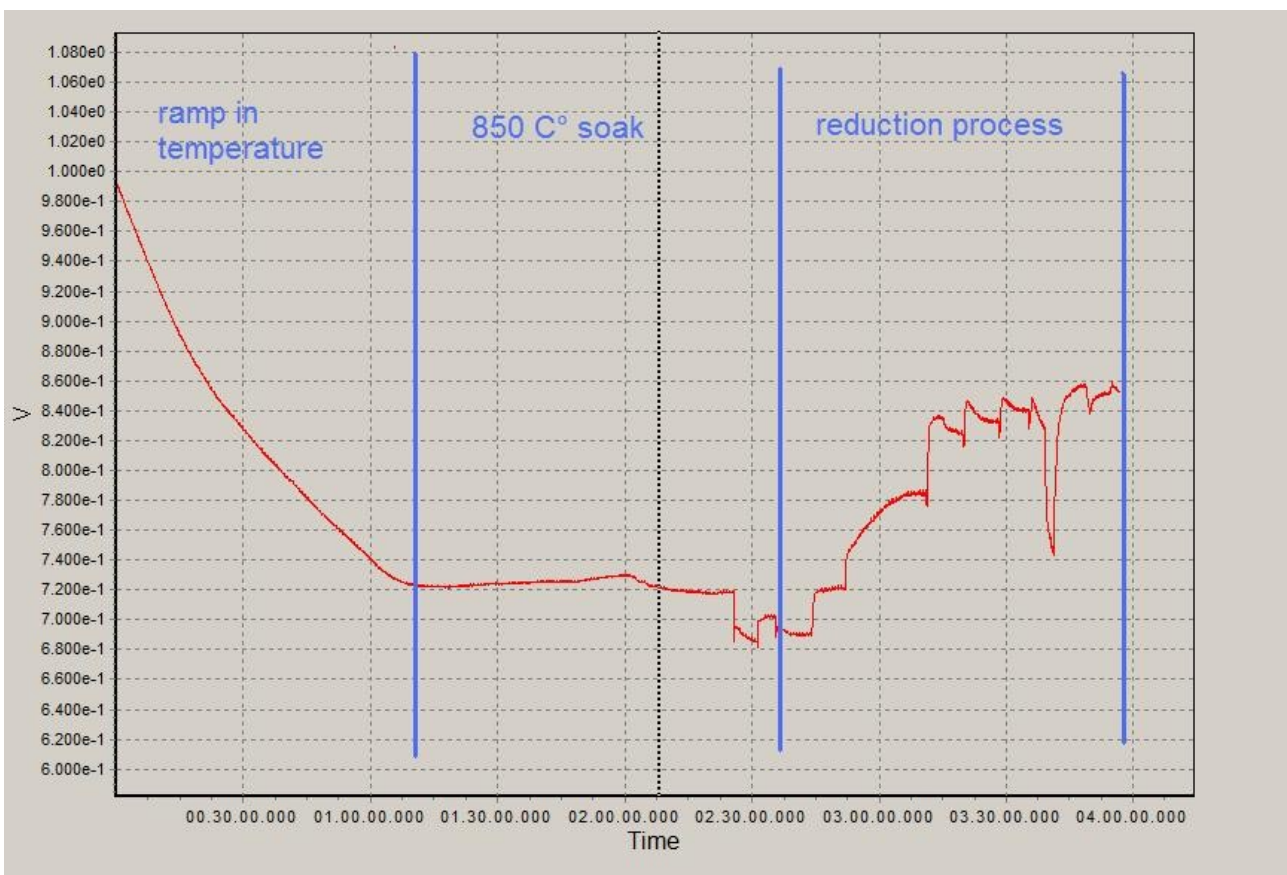
The gas composition is a lightly (and, by the way, safe) reducing atmosphere on anodic side, like 2 to 5% H<sub>2</sub> in N<sub>2</sub> dry, while on cathodic side it can be air.

Note that this measure gives us enough hydrogen for start a reducing process but not enough to reach the cathode electrode in case of leak without being transformed to water first.

The forming of the seal request an end point of 900-930 C° to be effective, with a soak period of at least 15 min. before descending, allways with a driven ramp of the same slope, to the operating temperature of about 800-850 C° depending on the cell's specs. Due to the non tightness of the seal during this ramp we use the same flow on both sides, but to avoid too much water forming we will not strongly overflow the sample with gas: a 50-60 ml/min per side are enough for the start up to the soak and the return to 800 C° plateau.

Is always a good idea to monitor the OCV during all the process: this gives an early warning on problems and a good control of what is going on in the sample.

A typical plot for a complete sample's conditioning is depicted here:



the ramp was not monitored from the start due to the fact that below 300-400 C° the impedance of the sample is too high to be monitored even with a very good electrometer input.

The peak temperature reached was 900 C° , kept for about 15 min around the blue line between the ramp and the soak step.

Is easy to see the descent of the OCV in rising the temperature same as to evaluate the losses that are making the sample running below 1 volt.

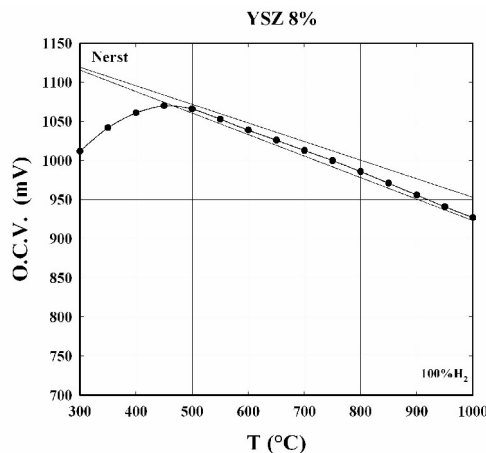
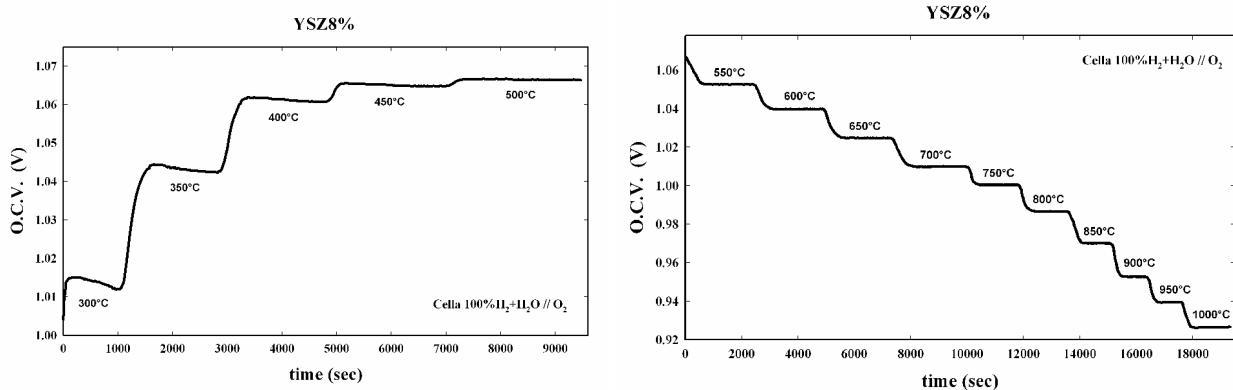
The slow rise in temperature cannot be considered enough to condition the sample to be ready for complete reduction, so a soak for a long period at operating temperature and low hydrogen is recommended.

In the previous picture about one hour and a half was spent in it.

To complete the description of the very early moments in starting a cell, see in the following plots the OCV behaviour of Zirconia vs temperature.

The first is the low temperature part while the second is the higher part of it: all the data are collapsed in a single plot with the comparison to the Nerst line

Note that the deviation of the value from theoretical is mainly due to the finite impedance of the multimeter that reads a generator with extremely high series impedance



These plots are Copyright Dr. Gaetano Chiodelli , measured at CNR-IENI in Pavia (Italy): we thank for the kind contribution.

### Seal testing:

a common question is to know if the gold ring is working or not, being it the main factor of uncertainty in the test.

To check for it, after the peak temperature was reached, one can quickly cut the gas supply on the air or hydrogen side, and see if the gas output on that side is no longer passing by (a simple bubbler to check is just enough).

Remember that no internal pressure is present, so avoid long water columns for bubbling. In case a significant leak is detected, one can, depending on the sample, increase the seal temperature a little to try to fix it, or just leave it and play with the flows once the flux is restored.

During those trials the OCV collapses, due to the unbalanced operation and sometimes don't return back completely in short time: for this reason is better to do not let this condition for more than 30-60 sec before restoring the other gas.

The complete recovery of the OCV can take more than 10 minutes, so , be prepared to it.

### The reduction process :

at the end of the soak step the reduction process that brings the cell to the working conditions can be started.

To fix the essential points:

- the reduction process changes the presence of Hydrogen in the anode gas to reach the operating status at 100% hydrogen or other similar limit.
- A progressive introduction of H<sub>2</sub> is due for the correct reduction of the electrode in the inner layers of it
- a time scheduling with ratio and time is depicted here, but the observation of the samples' ocv is sometimes more important for a correct process progression.
- A sample not correctly reduced can bring to reduced performances , delamination of the electrodes or other injuries and , in general can be detected through a performance increase of the OCV at hydrogen's reduction.
- Is not uncommon to see a not well reduced sample “collapsing” , with a dramatic OCV drop: in this case restarting the procedures after a soak at 5% H<sub>2</sub> for one hour can save it for a while but the endurance of it is not guaranteed.

A general starting point to work can be the following:

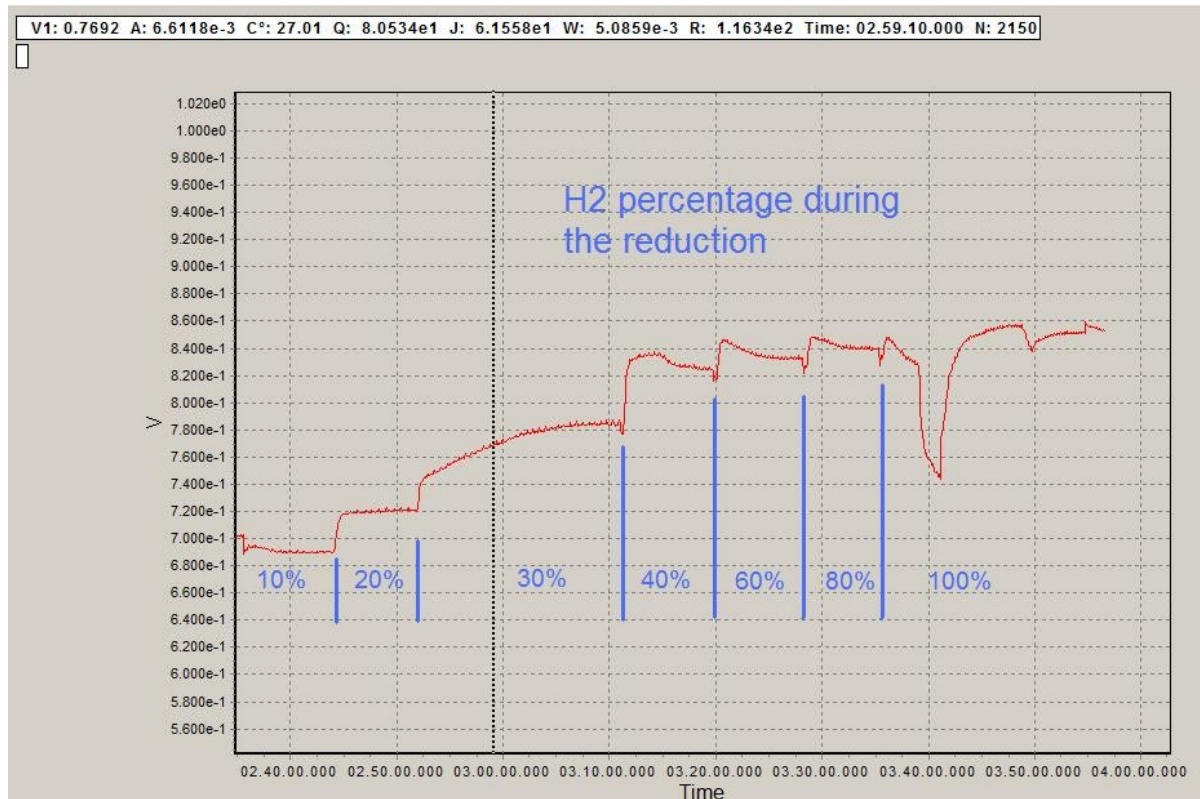
- phase 1 H<sub>2</sub> 10% 10 min. (rest N<sub>2</sub> to match the flow requested)
- phase 2 H<sub>2</sub> 20% 10 min.
- phase 3 H<sub>2</sub> 40% 10 min
- phase 4 H<sub>2</sub> 60% 10 min
- phase 5 H<sub>2</sub> 80% 10 min
- working: H<sub>2</sub> 100%

another possible scale up is

- phase 1 H<sub>2</sub> 10% 8 min. (rest N<sub>2</sub> to match the flow requested)
- phase 2 H<sub>2</sub> 20% 8 min.
- phase 3 H<sub>2</sub> 30% 8 min
- phase 4 H<sub>2</sub> 40% 8 min
- phase 5 H<sub>2</sub> 60% 8 min
- phase 5 H<sub>2</sub> 80% 8 min
- working: H<sub>2</sub> 100%

this theoretical profile can work correctly or not depending on the sample's preparation, type, temperature and other factors.

If we take the picture in the example we can see some interesting behaviours to follow.



The profile chosen was the second, but the behaviour of the sample gave us some signals that some steps were still in evolution at the end of the given time.

For this reason we deliberately left the sample at 30 % concentration up to the point we saw a reasonably asymptotic behaviour .

The other steps reached the level in a shorter time , showing some hydrogen excess at the start of the step.

The ocv drop during the latest part of the plot is (just to cite it) due to the lack of gas on the cathodic side.

The sample you see in the picture was then tested with success during a couple of days, showing good stability and current capabilities: in other words, it was correctly reduced.

### The test of the sample

Now that your sample is ready you can play with it in many ways, but is a good practice to let it run at reasonable current levels for a while in order to finalize the activation of all the parts: an overnight run at 0.6 V can do the job, with overall gas flows of about 200- 300 ml /min p, some er side and humidified anodic gas .

Regarding the water and the water condensation in the bottom of the cell is better to understand how much water we must expect .

In fact is not uncommon to see water out of the anodic compartment, and small drops are enough to change the gas pressure during the evacuation of them, making the ocv very unstable.

If the quantity exceed what can be easily handled one can choose between different solutions:

- heat up the exhaust path and the cell's body
- place a condensation filter just after the cell, in a position that makes the water dropping by gravity

In any case, when you see OCV bumps, try first to check the exhaust path before counteracting with gases: once again, a good couple of bubblers can monitor the flux in a convenient way.

## Conclusions

Well away to be exhaustive, the note gives to the reader some of the “practical feelings” we experience all the times, and be prepared that most of the time you will see a different behaviour from samples supposed to be “identical”.

The gold ring sealing method is not suited for low temperature SOFC and exhibits more leaks than any other.

On the other hand, is practical, very fast to form, and is able to give you back the sample in one piece (a couple of time we have re-run the same sample just to prove the concept). We expect comments on this application note and we warmly invite all you to participate with your experience to this item.

The mail to use for posting the notes is [tech@mmates.com](mailto:tech@mmates.com)

Our commitment is to give you a second release of this note after the received feedbacks will be enough to be published again.

## Acknowledgments

I would like to thank all the people made us growing in this field.

Is difficult to name them all, but, I need to cite Cyrille Deces-Petit and Rob Hui of NRC Vancouver and Gaetano Chiodelli of CNR-IONI Pavia as our main references.

Thanks to everybody had discussed about this with us.