



# D1.1 – Test protocol established among consortium partners

## PROJECT INFORMATION

|                           |   |
|---------------------------|---|
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| PROJECT FULL TITLE        | Low Cost Interconnects with highly improved Contact Strength for SOC Applications |
| PROJECT ACRONYM           | LOWCOST-IC  |
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## DELIVERABLE INFORMATION

|                       |   |
|-----------------------|---|
| DELIVERABLE N°        | D1.1  |
| DELIVERABLE TITLE     | Test protocol established among consortium partners                 |
| WP NO.                | 1   |
| WP LEADER             | Henrik Lund Frandsen  |
| CONTRIBUTING PARTNERS | DTU, CU, FZJ, SAN, SUN, SOL   |
| NATURE                | Report  |
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| CONTRACTUAL DEADLINE  |   |
| DELIVERY DATE TO EC   |   |

## DISSEMINATION LEVEL

|    |  |   |
|----|--|---|
| PU | Public   | X |
| PP | Restricted to other programme participants (incl. Commission Services)           |   |
| RE | Restricted to a group specified by the consortium (incl. Commission Services)    |   |
| CO | Confidential, only for the members of the consortium (incl. Commission Services) |   |

# 1 Evaluation of corrosion resistance and Cr vaporization

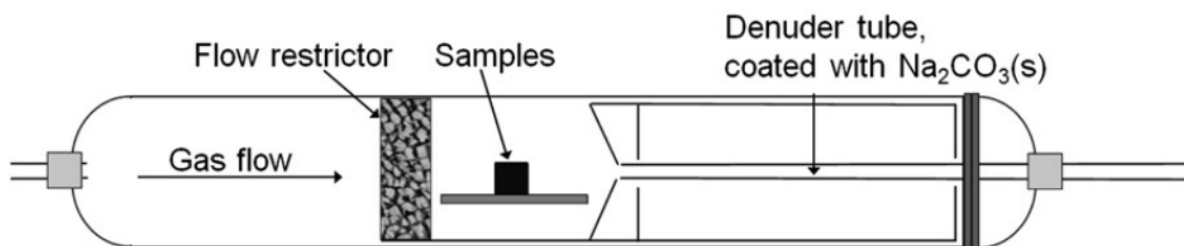
## 1.1 Coupon testing (WP2)

The following laboratory experiments at component level will be performed at Chalmers University

1. Quantification of chromium evaporation
2. Mass gain measurements
3. Post analysis of oxidized samples (XRD, EDX/SEM, FIB and TEM)

The materials will be cut into 15 x 15 mm<sup>2</sup> coupons. The uncoated samples are ground to 2400 grit before any further handling whereas the coated samples will be handled in the as-received state. All the samples will be cleaned in acetone for 20 minutes using an ultrasonic bath to dissolve any grease or organic material present on the surface. The samples are then dried before being cleaned in ethanol for 20 minutes using an ultrasonic bath. The dried samples are stored in individual sample bags. The initial mass of the samples is recorded using Mettler Toledo six decimal scale.

The investigations will be carried out at 750° C and 850° C in a horizontal tubular quartz reactor shown in Figure 1. Before the exposure, the hot zone of the furnace is located with the help of an S type thermocouple. The temperature of this zone is set as required. The temperature of the hot zone is let to stabilize and monitored for 5-6 hours before starting the exposure.

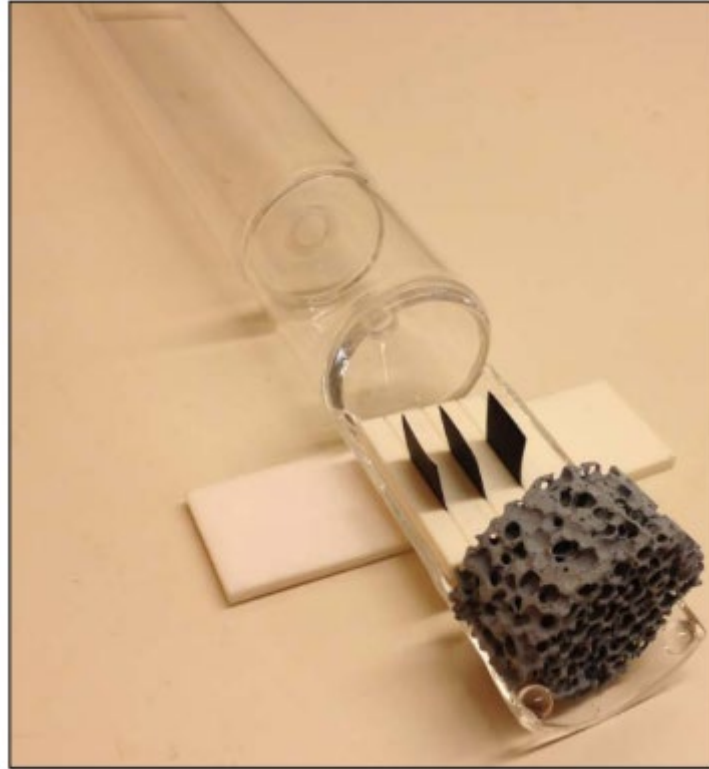


**Figure 1: Schematic drawing of the reaction chamber used for the exposures**

The samples are placed in an alumina holder with three slits, which is placed in the hot zone of the furnace. The slits and the samples are placed parallel to the flow as shown in figure 2. In order to minimize the natural convection, a porous silicon carbide flow restrictor is placed in front of the samples. This ensures a more uniform flow pattern around the sample surfaces.

The water content in the exposure atmosphere is usually maintained at 3% H<sub>2</sub>O. To maintain 3% H<sub>2</sub>O in the atmosphere, the schematic setup shown in figure 3 is used. The gas is bubbled through a distilled water bath which is maintained at 30°C. The gas exits the water bath through a condenser, which is set at 24.4°C using a heating circulator. The dew point of 24.4°C corresponds to 3% water vapor in the gas. The excess water vapor in the gas condenses on the walls of the condenser. All the hoses connecting the condenser exit to the furnace are set to 60°C with the help of heat cord to make sure that the water vapor in the gas doesn't condense on their walls. Moreover, all the tubing and the condenser are properly insulated to reduce the effect of external conditions. The water

vapor content in the gas is measured and recorded using a hygrometer (Optidew Vision dewpoint meter, Michell Instruments) at the exit of the furnace tube.



**Figure 2: Silica inner tube mounted with three samples and a SiC foam behind the samples**

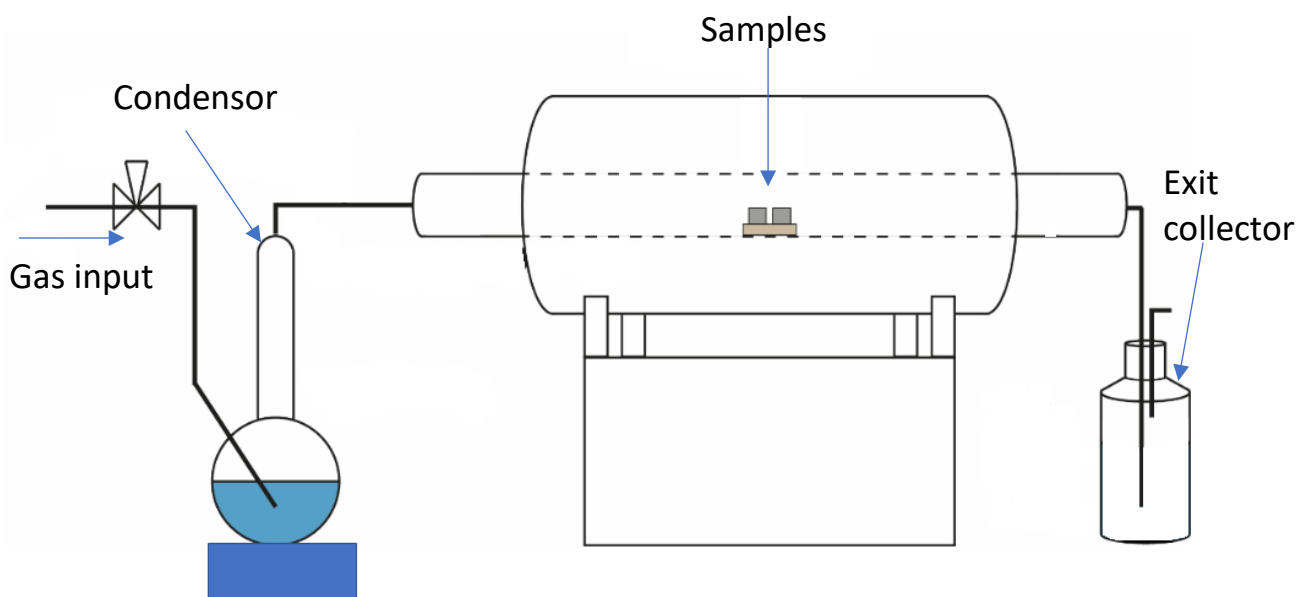


Figure 3: Schematic diagram of the experimental setup used

### 1.1.1 Simulated cathode side exposures:

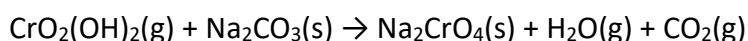
The samples will be exposed to an air-3% H<sub>2</sub>O atmosphere. The flow rate is set to 6000 sml min<sup>-1</sup> to ensure a flow-independent regime in the reactor. The reaction chamber is made of quartz glass.

### 1.1.2 Simulated anode side exposures:

The samples will be exposed to an Ar-5% H<sub>2</sub> -3% H<sub>2</sub>O atmosphere. The flow rate is set to 1000 sml min<sup>-1</sup>. The reaction chamber in the anode side exposures is made of alumina to circumvent the problem of silica vaporization in quartz glass.

## 1.2 Cr vaporization measurements (the denuder technique):

The denuder technique is used to collect volatile chromium (VI) species. This technique is based on the reaction between sodium carbonate and volatile chromium species. Figure 1 shows that a denuder tube (made from quartz) is placed behind the samples to act as the reactor outlet. The inside of the denuder tube is coated with Na<sub>2</sub>CO<sub>3</sub>(s), and, as volatile Cr(VI) species, formed at the sample surface, are transported with the gas stream through the coated denuder tube, sodium chromate is formed according to the reaction



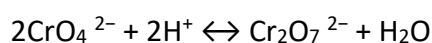
Each of the chromium vaporization measurement contains three samples placed in the alumina sample holder which is placed in the hot zone of the furnace. The denuder tube coated with Na<sub>2</sub>CO<sub>3</sub>(s) is placed at the outlet of the reactor. The outlet of the denuder tube is connected to a dry gas wash bottle to collect any flaked Na<sub>2</sub>CrO<sub>4</sub> and unreacted Na<sub>2</sub>CO<sub>3</sub>(s). The denuders and wash

bottles are replaced at regular interval which depends on operating temperature and coating. Due to higher Cr evaporation in the uncoated samples, the denuders are replaced frequently. The denuder and gas wash bottle is leached with water to collect the  $\text{Na}_2\text{CrO}_4$  and unreacted  $\text{Na}_2\text{CO}_3$ . The amount of vaporized Cr is then quantified using spectrophotometry (Evolution 60S, Thermo Scientific).

This is a simple, but also a very efficient, method to collect volatile chromium species. By using the denuder technique, collection efficiency of  $95 \pm 5\%$  can be achieved. The second advantage of this technique is that the denuder tube can be replaced regularly and rinsed with water, without affecting the samples.

#### *Quantification:*

The maximum light absorbance for chromate in solution is at a wavelength of 370 nm. The following equation shows the equilibrium reaction between chromate and dichromate.



It is important that the equilibrium of this reaction shifts towards the predominance of chromate ions since a dichromate ion does not have the same maximum absorbance wavelength as chromate ions. The 100% predominance of chromate ions requires a  $\text{pH} > 9$ . The sample solutions from the leached denuders are sufficiently alkaline for the equilibrium to shift towards chromate ion predominance, due to the high alkalinity of sodium carbonate from the denuder tubes.

Calibration of the instrument with a standard chromate solution showed a linear dependence on concentration, which is in good agreement with the Lambert-Beer relation

$$A = \varepsilon * l * c$$

where  $A$  is the absorbance,  $\varepsilon$  is the molar absorptivity,  $l$  is the path length of the light through the solution, and  $c$  is the concentration. In this case,  $l$  is a constant since only one type of cuvette fits into the spectrometer, thus the absorbance dependence on concentration can be derived from the standard curve and expressed as

$$A = 0.0902 * c$$

if the concentration is expressed in weight ppm of chromium.

#### **1.2.1 Mass gain measurements:**

##### a) Discontinuous exposures:

The mass gain measurements use up to six coupons for coated samples. For the uncoated samples, only three coupons are used to reduce the effect of chromium evaporation on each other. The mass of the samples is recorded at regular intervals using a Mettler Toledo six decimal scale to monitor the oxidation rate. Thus, the samples undergo thermal cycling each time the samples are weighed.

##### b) Isothermal exposures:

Some experiments will also be carried out where the samples are only exposed once, to validate the use of discontinuous exposures. Additionally, the measurement of Cr evaporation are at isothermal exposures and give additional statistics on mass gain.

## 2 Evaluation of contact resistance

Measurements of the contact resistance, also known as the area specific resistance (ASR), will be performed at DTU. The ASR will be evaluated for the following interfaces:

- 1) Steel/coating/LSM contact plate
- 2) Steel/coating/contact layer/LSM contact plate

For these tests, coated steel sheets are cut to  $2 \times 4 \text{ cm}^2$  coupons and two 6 mm holes are drilled in the shorter ends for mounting purposes, as illustrated in Figure 4. Platinum wire ( $\varnothing$  0.3 mm) is flattened on one end and welded to each coupon along the shorter edge. For tests of interfaces 2), the cathode contact layer will be screen printed on top of the coated steel with an area of  $2 \times 2 \text{ cm}^2$ . Porous  $\text{La}_{0.85}\text{Sr}_{0.1}\text{Mn}_{1.1}\text{O}_3$  (LSM) ( $20 \times 20 \times 1 \text{ mm}^3$ ) plates spray coated with a 50–60  $\mu\text{m}$  layer of LSM (89 wt%) and  $\text{Co}_3\text{O}_4$  (11 wt%) slurry mixture are used as contacting plates and represent a typically used oxygen electrode material in SOC stacks. The LSM plates are stacked between the steel plates. A single unit in this stack is illustrated in Figure 4. Gold foil (0.3 mm) connected to gold wires, is placed on the top and bottom of the stack to distribute the current, and a dead load of 7 kg is put on top to ensure good contact between the different layers.

The stacks are heated to 750 or 850 °C following the thermal profile in Figure 5. The slow initial ramp rate and dwells at low temperature are included to burn off the organics in the contact layers. A measurement current of 2 A, corresponding to  $0.5 \text{ A/cm}^2$ , is applied once the stack has reached the dwell temperature (750/850 °C). The ASR is monitored continuously (every 15 min) during aging by recording the voltage drop between two Pt-wires, as illustrated in Figure 4. The ASR is calculated according to:

$$ASR = \frac{\Delta V_{sample}}{I} A_{sample}$$

Where  $\Delta V_{sample}$  is the voltage drop,  $I$  is the current and  $A$  is the area across which the current is passed. After aging for 3000 h at the dwell temperature, 50 thermal cycles are performed between the dwell temperature and 200 °C with a cooling and heating ramp of 120 °C/h.

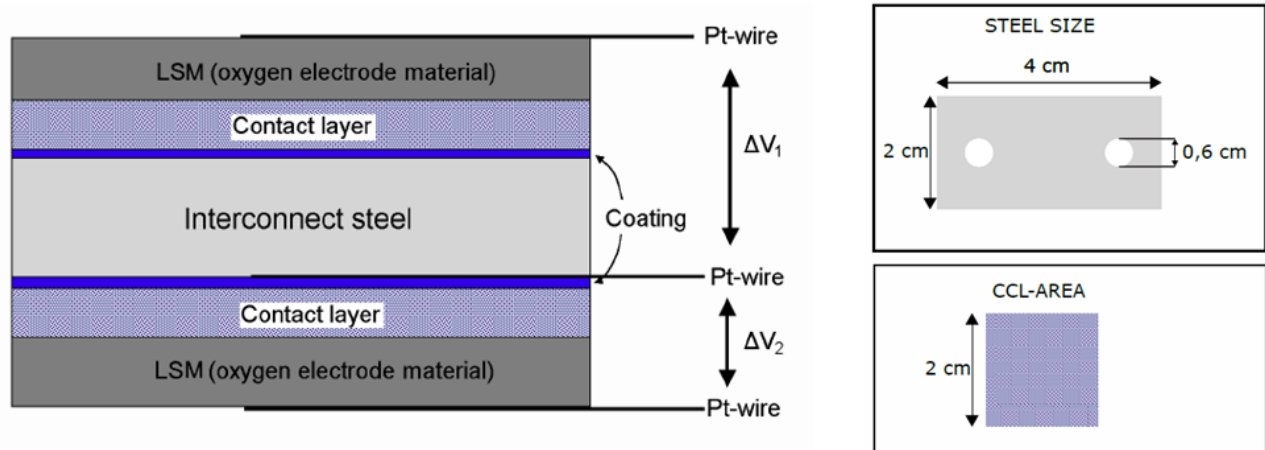


Figure 4: Set-up for area specific resistance measurement

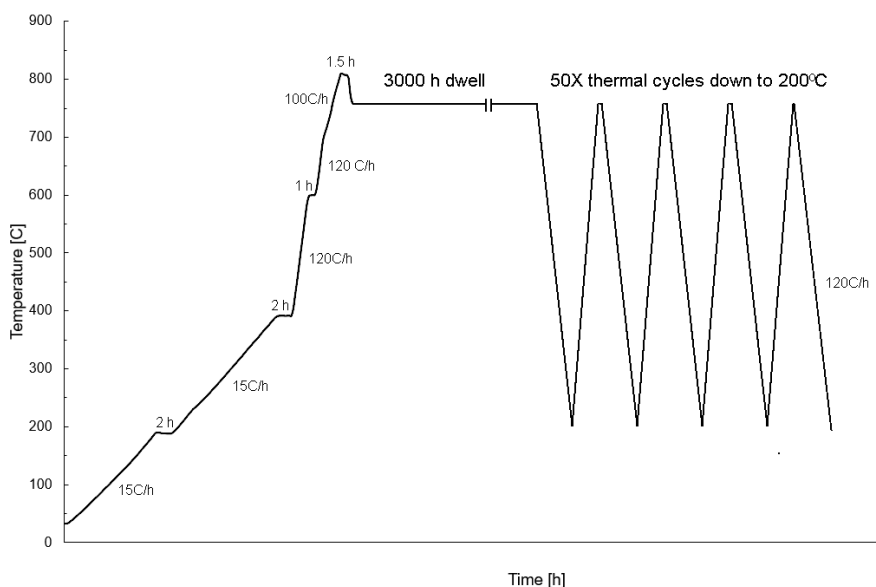


Figure 5: Thermal profile for ASR tests (here shown for the case of dwell at 750 °C)

### 3 Evaluation of fracture energy

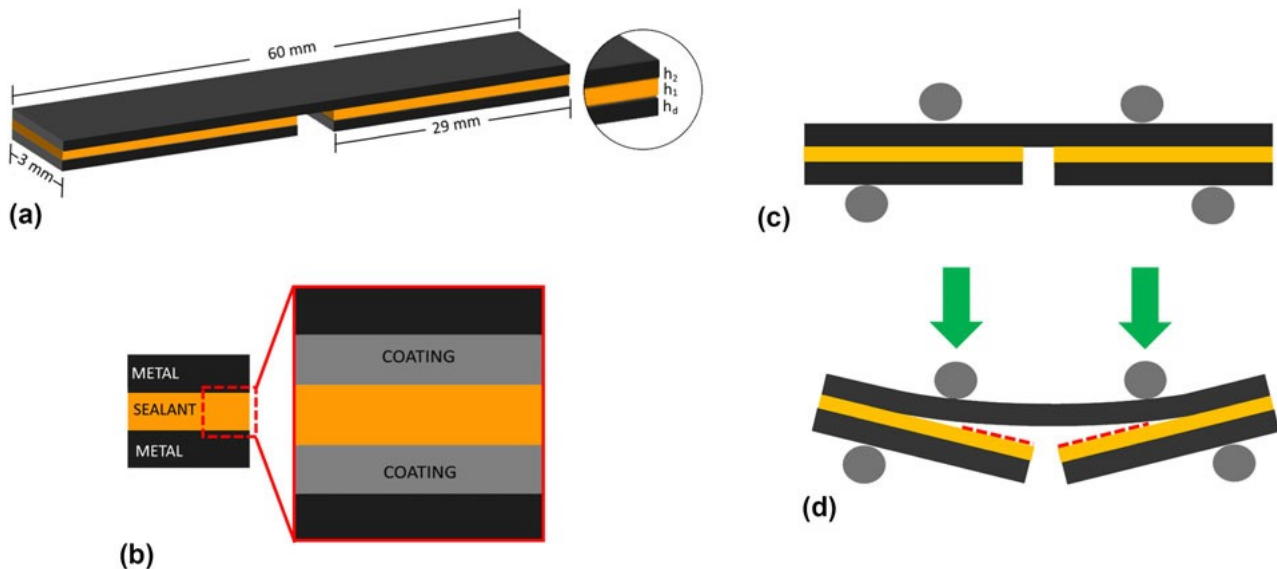
To evaluate the fracture energy needed to generate a crack between surfaces in the solid oxide fuel cell stacks is measured by four-point bending using the Charalambides test geometry. In LOWCOST-IC project the fracture energy will be measured in the interface between the coating and the steel and between the coating and contact layer after various exposures. The Charalambides test geometry and the testing procedure is presented briefly in the two following sub-sections, and details on the method and theory behind can be found in Ref. [1–3].

### 3.1 Sample preparation

The overall geometry of the samples used in the fracture energy characterization is shown in Figure 6a. The symmetric configuration is chosen to avoid the influence of residual stresses. The 300-500  $\mu\text{m}$  thick interconnect steel is used as substrates transferring the load in the bending experiment. The steel samples are etched to shape from a larger sheet metal supplied by partners (APE, SMT). After shaping, the samples are cleaned in acetone and ethanol for 10 min in an ultrasonic bath.

The layers between the two metal substrates are chosen from on the interface of interest:

1. For testing the coating / steel interface, the layers in the interface are as shown in Figure 6b. The glass is assumed to be the tougher material, and the failure to occur in the interface between the coating and the interconnect steel.
2. For testing the contact layer / coating interface, the glass in Figure 6b is replaced by a contact layer.



**Figure 6 (a) 3D sketch of the full sample geometry, (b) layers in each sample, (c) four-point bending loading configuration, and (d) failure mechanism during loading (from [1]).**

The glass used in these experiments is the DTU in-house fabricated glass, see Refs. [1,4]. Various reactive bonding contact layer compositions based on metallic Cu, Co and Mn powders will be tested. The in-situ oxidation will bond the two coated interconnects in the same manner as the glass. The glass and the contact layer will in the following commonly be referred to as the bonding agent.

The bonding agents will be applied by screen printing on the shorter metallic bars (Figure 6a) to ensure a notch without the bonding agent, as having this in the notch can make it difficult to initiate the crack (resulting in plastic bending of steel substrates and unreliable measurements).

The sandwiched samples will be heat-treated (“sealed”) under a load of  $\sim 20 \text{ N/cm}^2$  applied by a hydraulic piston and distributed by two alumina plates.

The bonding agents will be heat treated using following heating profiles:



- Glass: ramping from 20 to 600 °C at 100 °C/h, holding for 1 h, ramping from 600 to 700 °C at 100 °C/h, ramping from 700 to 800 °C at 50 °C/h, holding for 1 h, and then cooling down to room temperature.
- Contact layer: ramping from 20 to 600 °C at 100 °C/h, holding for 1 h, ramping from 600 to 700 °C at 100 °C/h, ramping from 700 to 800 °C at 50 °C/h, holding for 10 h, and then cooling down to room temperature.

To ensure a good statistical representation of the fracture energy, five samples for each configuration, i.e. configuration and exposure condition, will be tested.

### 3.2 Test method

The samples are tested in four-point bending (Figure 6c) in a rig built in-house at DTU [5]. The unbroken sample will be increasingly loaded and bend until the stress concentration at the interface becomes sufficiently large to propagate two cracks, one to either side of the notch, in the interface between the layers, see Figure 6d.

The distance is 25 and 50 mm between the inner and outer pins, respectively (Figure 6c).

After the crack has formed, the stiffness decreases, resulting in a constant load plateau,  $P$ , with increasing bending. The load plateau is used to determine the fracture energy,  $G_c$

$$G_c = \frac{M_b^2 (1 - \nu_2^2)}{2 E_2} \left( \frac{1}{I_2} - \frac{1}{I_c} \right)$$

where

$$M_b = \frac{Pl}{2b}$$

where  $E_2$ ,  $\nu_2$  and  $I_2$ , are the Young's modulus, Poisson's ratio and second moment of area of the through-going substrate of the interconnect steel, respectively.  $I_c$  is the combined second moment of area of the substrates ( $d$  in Figure 6b) and the bonding agent.

The second moment of areas for the substrate is calculated by

$$I_2 = \frac{h_2^3}{12}$$

where  $h_2$  is the thickness of the substrate.  $I_c$  is given by:

$$I_c = \frac{h_2^3}{3} + \kappa \frac{h_1^3}{3} + \mu \left( \frac{h_d^3}{3} + h_d^3 h_1 + h_1^2 h_d \right) - \frac{[h_2^2 - \kappa h_1^2 - \mu (h_d^2 + 2 h_1 h_d)]^2}{4 (h_2 + \kappa h_1 + \mu h_d)}$$

where index 1 refers to the stiffener (the short metal strips).  $\kappa$  is the ratio between the stiffness of the substrate and the stiffener, which are identical here, and thus 1, and  $\mu$  is the ratio between the stiffness of the substrate and the glass-ceramic layer

$$\mu = \frac{E_d (1 - \nu_2^2)}{E_2 (1 - \nu_d^2)}$$

where  $E_i$  and  $\nu_i$  are the Young modulus and Poisson's ratios of the  $i$ 'th layer.

## 4 Stack testing

### 4.1 Defined standardized testing protocols

During the LOWCOST-IC project, stack tests will be carried out. To be able to compare the results from various stack designs and material combinations, testing protocols were defined to be used by SOLIDpower, FZ Jülich and Sunfire.

The stacks that will be tested are either short stacks (6-cells for SOLIDpower, 10-cells for Sunfire), which will be tested within an oven, and full stack tests, which are tested in a hotbox. There will be tests for steady state operation and thermal cycles. Due to the different stack design, not all parameters can be standardized as will be given in the next chapters.

### 4.2 General parameters

All tests will be carried out in  $H_2/N_2$  atmosphere. The only exception for this is when newly developed coatings on the fuel side will be evaluated. If that is the case during the LOWCOST-IC project, a minimum test of 500 h in steam reformat and/or SOEC-mode is mandatory to ensure the coating properties also under different atmospheres.

The quality control of the several stack suppliers (IV-curve, electrochemical leakage tests etc.) will be done according to the supplier specifications to ensure comparability to previous tests. Also, the ASR-calculation will be done according to the specifications of the stack supplier to be able to compare those results with previous tests.

### 4.3 Steady State Operation

For steady state operation, only the fuel conversion and the air source can be standardized. Temperatures as well as current densities have to differ because of the various stack designs.  $H_2/N_2$  atmosphere must be different due to test bench constrains. All parameters of the partners and the ones that will be used within LOWCOST-IC are given in Table 1.

**Table 1 Parameters for steady state operation**

|                                     | Sunfire                    | SOLIDpower                                     | FZJ             | Used for LOWCOST-IC |
|-------------------------------------|----------------------------|--|-----------------|---------------------|
| FU / %                              | 75                         | 80   | 40              | 80                  |
| Current density / A/cm <sup>2</sup> | 0.23                       | 0.41   | 0.5             | not standardized    |
| H <sub>2</sub> / %                  | 40                         | 60   | 100             | not standardized    |
| N <sub>2</sub> / %                  | 60                         | 40   | 0               | not standardized    |
| T_Max / °C                          | 860                        | 750  |                 | not standardized    |
| Air                                 | pressurized or ambient air | pressurized ambient air<br>OxU (10,3%@<br>33A) | pressurized air | pressurized air     |

#### 4.4 Hotbox tests (full stack)

For hotbox tests, the minimum temperature to be reached as well as the gases can be standardized. Load operation is given by the quality assurance measurements required by the supplier, and the cooling ramp is limited by the test bench.

The load operation during thermal cycles will be done according to the parameters given in chapter 4.3.

**Table 2 Parameters for thermal cycling**

|                            | Sunfire                    | Solidpower                           | FZJ                 | used for LOWCOST-IC |
|----------------------------|----------------------------|--------------------------------------|---------------------|---------------------|
| T_Min / °C                 | 100                        | 80-100                               | 100 or 200          | 100                 |
| load operation time / h    | 4                          | 20                                   |                     | not standardized    |
| ΔT <sub>up</sub> / K/min   | 5                          | 1.8                                  | 2~10                | not standardized    |
| ΔT <sub>down</sub> / K/min | given by test bench        | 1 (limited by the test bench)        | given by test bench | given by test bench |
| fuel                       | forming gas                | 60%H <sub>2</sub> /40%N <sub>2</sub> | forming gas         | forming gas         |
| air                        | pressurized or ambient air | pressurized or ambient air           | pressurized air     | pressurized air     |

## 5 Post-test analysis

### 5.1 Post analysis of oxidized samples:

#### 5.1.1 X-ray diffraction:

The crystal structure of a flat sample can be determined using X-ray diffraction. This is useful to characterize the different oxide phases grown on metal samples. X-ray diffraction is based on the constructive interference of monochromatic X-rays that occurs at certain angles when scattered by a crystalline material. Diffracted constructive interference occurs at certain integer values ( $n$ ) and is dependent on an angle ( $\vartheta$ ), the wavelength of the X-ray ( $\lambda$ ), and the distance between lattice planes in the crystal ( $d$ ) and can be expressed by Bragg's law:

$$2d \sin\theta = n\lambda$$

A grazing incidence diffractometer (Siemens D5000) will be used. This kind of setup allows for the characterization of thin films, which is useful for investigating oxide scales grown on metals.

#### 5.1.2 Scanning electron microscopy (SEM):

SEM is used to characterize the samples after exposure. The main signals of interest are backscattered electrons, secondary electrons, and X-rays. Mainly, a FEI Quanta FEG 200 ESEM and a Zeiss LEO ULTRA 55 FEG-SEM will be used in this project.

#### 5.1.3 Transmission electron microscopy (TEM)

Transmission Electron Microscopy (FEI TITAN) will be used on selected samples in order to acquire information about microstructure, chemical composition and crystal structure with very high spatial resolution. Prior to the TEM analysis, an electron transparent specimen must be prepared, which is usually done by FIB milling and lift-out technique.

#### 5.1.4 Broad ion beam (BIB)

Preparation of cross sections by ion milling has several advantages compared to traditional methods like mechanical polishing, such as less mechanical damage on the cross-section surface, cracks and voids are not filled with polished material, and ion milling does not leave abrasive artefacts on the surface. For BIB milling, argon ions are utilized to mill deep into the sample and thus create a smooth surface that can later be analyzed in the SEM. A Leica EM TIC 3X which is equipped with three argon ion guns will be used. Before the milling process, a low speed saw with a diamond blade will be used to cut the sample in half to enable BIB cross sections from the center of the sample and not from the edges.

#### 5.1.5 Focused ion beam (FIB)

A focused beam of accelerated gallium ions (FIB) can be used for preparing cross sections of samples with very fine polishing. In combination with an SEM, it is possible to simultaneously image and

choose specific spots on a sample to mill a cross section. This makes it possible to get cross-sectional information about micrometer scale features. An FEI Versa 3D DualBeam (FIB/SEM) will be used on selected samples when mechanical polishing is not possible or special micrometer scale features are of interest.

## Acknowledgment



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