



Development of porous metal supports

Editorial

The 1st of December 2011 marked the start of the METPROCELL project: **Innovative fabrication routes and materials for METal and anode supported PROton conducting fuel CELLS**. It is a collaborative project funded by the [Fuel Cell and Hydrogen Joint Undertaking](#) (FCH JU) where 8 partners work together to develop a new generation of intermediate temperature fuel cells based on the Proton Conducting Fuel Cell technology.

This report summarizes the most outstanding results collected in the frame of work package 4 (WP4) within the task related to the development and characterization of porous metal supports (Task 4.1).

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1. Summary

This report summarized the most outstanding results collected in the frame of work package 4 (WP4) focused on the DEVELOPMENT OF LAB-SCALE CELL COMPONENTS, and specifically within the task dedicated to the development and characterization of metal porous supports for PCFCs.

Brief description of the state of the art and the innovation brought:

Tape casting is a well-established technology for making thin structures of ceramic materials. This is also possible with metals but there are a few challenges associated with the use of metal powders. These challenges are associated with the short stability of the slurry (fast sedimentation) due to the higher densities of the metals and usually much bigger particle sizes. Another challenge is associated to the binder selection and binder burnout to avoid carbide formation in the stainless steel. METPROCELL's partner, Höganäs AB (HOGANAS), worked with this technology since 2007 and has a couple of solutions depending on the type of problems that arise. Changing metal powders (chemical composition, particle size distribution, morphology) usually means new challenges and that the recipes must be changed. For HOGANAS, tape casting of metals is rather "state of the art" based on know-how obtained since 2007 and the tape casting of MW1-MW8 materials was considered to be rather straight forward. It is when thin structures shall be made that challenges arise. Up to our knowledge, there are only a few other players doing porous metal powder plates by tape casting (e.g. Plansee and Jülich).

Some of the alloy compositions can be considered to be new (at least for this application). However, if they shall be interesting they must add some extra value to the application. To explore the potential of the selected alloy compositions is one of the goals in METPROCELL.

2. Development of porous metal supports

The METPROCELL project aims to develop innovative fabrication routes with new electrolytes and electrode materials for building cost effective and durable Proton Conducting Fuel Cells (PCFCs). One of the proton conducting cell configurations has been a metal supported cell which has the possibility to be produced by different methods. HOGANAS' role in METPROCELL is to supply sintered porous metal powder supports which will be used for subsequent deposition of the ceramic layers (anode, electrolyte, cathode and if needed barrier layers). The TEC (Thermal Expansion Coefficient) of the porous metal support must match the TEC of the electrolyte in order to avoid crack formation in the electrolyte, which will cause cell destruction. The TEC of the electrolyte materials is around $10 \cdot 10^{-6} \text{ K}^{-1}$ which is why in principle, among the stainless steels, only ferritic stainless steels (Iron Chromium steels) have expansion coefficients that can match the TEC of the electrolytes. The work in METPROCELL has therefore been focused on iron chromium steels and modifications thereof. The porous metal support must also have a good high temperature oxidation resistance. High nickel containing austenitic stainless steels or super alloys (Ni based alloys) are known and proven to be oxidation resistant but have been avoided due to the much higher TEC ($>14 \cdot 10^{-6} \text{ K}^{-1}$). Al or Si in the stainless steels are also known to give good high temperature oxidation resistance. However, addition of Al has been avoided due to formation of an electrical insulating Al_2O_3 scale, which would decrease the cell performance due to higher electrical resistivity. For the same reason, the target silicon level has been as low as possible to avoid an insulating SiO_2 subscale below the chromia scale.

In the METPROCELL project, stainless steel powders with eight different alloy compositions were manufactured by water atomization at HOGANAS. The material compositions are summarised in **Table 1**.

Table 1: Chemical composition and designation of the metal powders used for the manufacturing of the porous metal powder plates.

| Name | Target composition | Fe | Analysed chemical composition, % | | | | | | | | | | | | |
|------|---------------------|------|----------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|
| | | | Cr | Ni | Mo | Mn | Cu | Si | Al | Nb | W | C | O | N | S |
| MW1 | Fe20Cr | Bal. | 20 | 0,07 | 0,02 | 0,03 | 0,03 | 0,08 | 0,00 | 0,02 | 0,00 | 0,02 | 0,54 | 0,05 | 0,01 |
| MW2 | Fe20Cr0.4Mn | Bal. | 22 | 0,03 | 0,01 | 0,23 | 0,02 | 0,08 | 0,00 | 0,02 | 0,00 | 0,04 | 0,58 | 0,07 | 0,01 |
| MW3 | Fe26Cr0.4Mn | Bal. | 27 | 0,01 | 0,04 | 0,30 | 0,00 | 0,08 | 0,00 | 0,02 | 0,00 | 0,03 | 0,72 | 0,17 | 0,01 |
| MW4 | Fe26Cr0.4Mn5W | Bal. | 28 | 0,01 | 0,01 | 0,31 | 0,00 | 0,09 | 0,00 | 0,02 | 4,19 | 0,01 | 0,65 | 0,21 | 0,00 |
| MW5 | Fe26Cr0.4Mn5Mo | Bal. | 28 | 0,01 | 4,39 | 0,46 | 0,00 | 0,09 | 0,00 | 0,00 | 0,52 | 0,01 | 0,70 | 0,13 | 0,00 |
| MW6 | Fe20Cr0.4Mn1Mo0.5Nb | Bal. | 20 | 0,02 | 1,37 | 0,46 | 0,00 | 0,07 | 0,00 | 0,57 | 0,05 | 0,01 | 0,73 | 0,10 | 0,00 |
| MW7 | Fe26Cr0.4Mn1Mo0.5Nb | Bal. | 26 | 0,01 | 1,06 | 0,46 | 0,00 | 0,08 | 0,00 | 0,81 | 0,00 | 0,02 | 0,74 | 0,10 | 0,00 |
| MW8 | Fe32Cr | Bal. | 32 | 0,02 | 0,08 | 0,09 | 0,00 | 0,07 | 0,00 | 0,13 | 0,00 | 0,01 | 0,79 | 0,08 | 0,00 |

The first material, designated MW1, was a water atomized iron-chromium alloy with 20 wt-% of chromium (**Figure 1**). In the second material, MW2, 0.4 wt-% manganese was added in order to form a chromium-manganese oxide spinel scale, which may provide higher resistance to chromium evaporation and a higher electrical conductivity than the pure chromium oxide scale. In the third material, MW3, a higher Cr content was used to increase the oxidation resistance as well as lowering the TEC. In the MW4 and MW5 materials, Mo and W respectively were added in high concentration in order to see if it was possible to decrease the TEC significantly. In MW6 and MW7 niobium was added with the purpose to improve the high temperature strength. Molybdenum has been added in order to take care of the low amount of silicon by forming Mo-Si rich areas. Molybdenum is also contributing to improved mechanical strength. Higher Cr contents have been added to reduce the TEC and to improve the oxidation resistance. With the higher amounts of Cr and some other alloying elements there is a risk for formation of sigma and laves phases that can influence the material properties negatively with time (e.g. embrittlement, lower corrosion resistance, TEC etc). DTU has evaluated the eight different alloys with respect to the risk for formation of sigma and laves phases and this is reported separately.

TEC measurements at HOGANAS of the different alloys in the interval 25-600°C led to values between $10.5\text{-}11\cdot 10^{-6}\text{ K}^{-1}$ except MW8, which showed a slightly lower TEC ($10.0\cdot 10^{-6}\text{ K}^{-1}$) probably due to the higher chromium content. Since the differences were small, the the values of TEC were not considered in the final selection of the material.

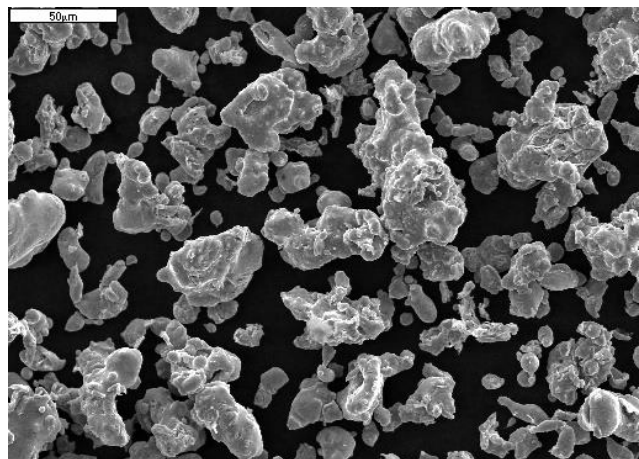


Figure 1. SEM picture of the MW1 powder. All MW1-MW8 powders look similar.

The eight different water atomized metal powders were shaped into thin planar green plates (115 x 115 mm) by tape casting and finally sintered in order to obtain the final porous metal powder plates. Plates of different thicknesses (0.2-0.8 mm) were manufactured for evaluation of the thickness required for the thermal spray deposition of the different cell components (even though an overall cell thickness of 0.3 mm or lower was initially defined by TOFC to obtain a higher power density per unit of volume). Tests at TECNALIA showed that a thickness of at least 0.6 mm was needed in order to avoid bending and deformation during detonation spraying, why all further manufacturing was focused on the thickness 0.6 mm.

Cell components are deposited on the lower side of the sintered tape, since a lower surface roughness is always obtained on it. Typical Rz values on the lower side are around 25 μm , while they are around 43 μm on the upper side.

Figure 2 shows a representative micrograph of the lower surface on a sintered support. According to TECNALIA, the surface roughness on the lower side is good enough for thermal spraying. Nevertheless, a post treatment method has been also investigated in order to decrease the surface roughness of the sintered porous metal supports when necessary. Rz values between 15-20 μm can be obtained after this treatment, even on the upper side. However, the porosity is reduced down to around 25% from 45%. The decision on the final support configuration will be done after cell performance tests at lab scale level. Sintered porous metal plates of all the materials have been sent to DTU for oxidation tests under real application conditions and to other partners for deposition of electrodes and electrolyte.

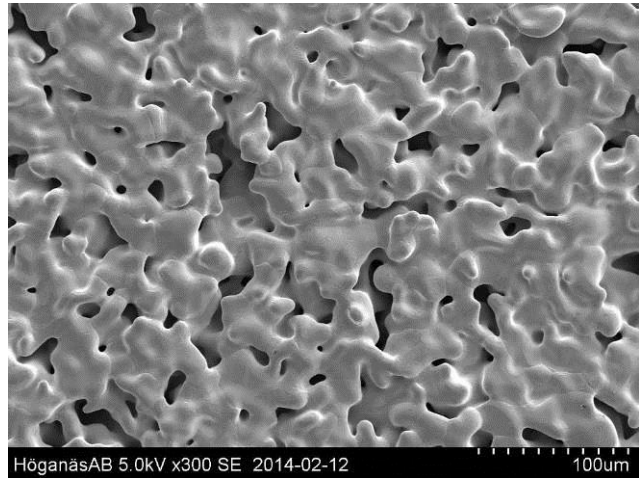


Figure 2. FEG-SEM pictures on the surface of a MW2 porous support sintered at 1250°C (lower surface).

3. Corrosion testing of the supports under service relevant conditions

Even though the metal support is meant to be placed on the hydrogen side in the cell, the atmosphere will not be pure hydrogen. It will be hydrogen containing different amounts of water vapour because humidification of the hydrogen anode gas will be performed in order to obtain stable and high electrolyte performance. Additionally, some O^{2-} transport through the electrolyte will take place giving water formation on the anode side. There will also be a relative increase of H_2O in the cell when H_2 is consumed. Finally, there are potential leaks in the cell that will give increased water content in the hydrogen anode gas. In the METPROCELL project it is considered that the hydrogen anode gas will be pure hydrogen humidified with 3% of H_2O . However, with time when efficient PCFCs (Proton Conducting Fuel Cells) exist the demand on use of reformat gas will come. This will increase the water content further in the anode gas and then carbon oxides will be present as well.

Oxidation tests at DTU for as sintered supports under real application conditions (humid hydrogen at 600°C) showed severe oxidation for the alloys with the lowest chromium

contents (20%, MW1, MW2 and MW6) and best results for MW4, MW5 and MW8. However, it was recommended that the high temperature oxidation resistance of the supports should be further increased. To improve the high temperature oxidation resistance, in principle two different methods can be used, i.e. a heat treatment step for formation of a resistant chromium oxide scale after sintering, or a wet post coating process adding elements to the surface that improve the oxidation resistance. The heat treatment for formation of a resistant chromium oxide scale has been performed in argon atmosphere with a low amount of oxygen at around 900°C and for different times. Argon has been used instead of nitrogen in order to avoid nitrogen pick-up in the porous stainless steel. The wet post coating has been performed by dip coating the porous metal substrates in a water based solution containing small precursor oxides of Zr, Ce or Y. After drying, the coated substrates have been calcined at 550°C. The weight has always been recorded for the as sintered substrates and after the different coating procedures.

With the heat post-treatment for formation of a chromium oxide scale the oxidation resistant increased tremendously, especially for the porous metal substrates with the lowest chromium content. After 450 h in humid hydrogen (4% H₂O/H₂) all samples had a weight increase below 0.4 wt%, which can be compared to the 17 wt% gain after 100 h for as sintered MW2 supports. The results showed that to obtain a consistent high temperature oxidation resistance quality, it is very important to have a controlled oxidation after sintering. However, as mentioned above, an alternative to this approach is the wet post coating. The post coating is preferred because it is easily performed, easily reproduced and may lead to even higher oxidation resistances than previous pre-oxidation method. Among the tested compositions at HOGANAS it seems that Y-based coatings may lead to the best results.

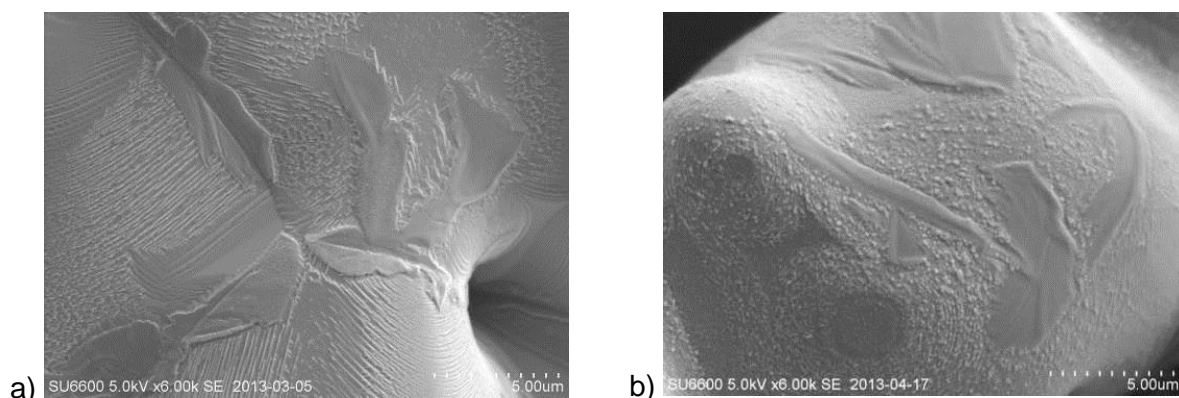


Figure 3. FEG-SEM pictures on the surface of **a)** as sintered MW2 and **b)** as prepared MW2 with Y-based coating).

Consequently a porous metal support consisting of MW2 with an Y-based coating (<0.3 wt% as prepared) can be a good substrate for metal supported PCFCs (Figure 3). With such a coating, the maximal weight increase is around 0.4% after oxidation tests at 600°C for 1500 h in humid atmosphere (for Y-based coatings applied by either HOGANAS' or DTU' method as shown in Figure 4).

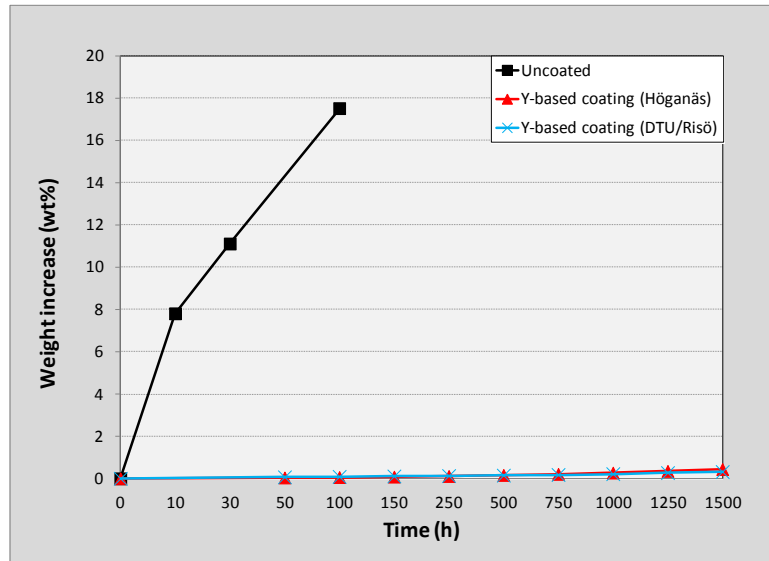


Figure 4. Weight increase after oxidation in humid H₂ (4% H₂O/H₂) at 600°C for 1500 hours for uncoated MW2 and MW2 coated with an Y-based coating. The Y-based coating has been performed by two different methods, one from HOGANAS and second from DTU. The results in the figure are from oxidation tests performed at DTU.

The selected support is

MW2<53 μm that is coated with an Y-based coating. The selection might change when further information is obtained from durability tests, cell manufacturing and testing.

Project details

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