A metallic seal for high-temperature electrolysis stacks

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Abstract

Gas tightness over a long period of time is a real challenge in high-temperature electrolysis. The seals must indeed be able to run at high temperature between metals and brittle ceramic materials, which is a major issue to be solved. The common sealing solution relies on glass-made seals, despite their low mechanical strength at high temperature. Metallic seals have seldom been used in this field, because their stiffness and their hardness require a much higher load to achieve the appropriate tightness.

In the French project ANR Pan-H/SEMIEHT, two different sealing solutions were investigated in two different locations of the GENHEPIS-G1 stack. Experiments were carried out with a glass-made seal between the cell and its ceramic support, and with metallic seals between the interconnect and the cell support, in order to seal the gas input and output as well as the cathodic chamber. An initial Garlock seal design has been optimised in order to decrease the seating load. Seals were also manufactured by Garlock. The C-shaped seals are made of two components: an Inconel-X750-made elastic inner part, and a specially profiled Fecralloy-made "soft" outer lining. The use of Fecralloy enables the generation of an alumina thin layer, which both protects the seal and eases disassembly. In this study, these seals were tested on specific equipments and on actual stacks. It is shown that they are tight enough to achieve the electrolysis tests at 800°C. Therefore a significant breakthrough in high-temperature electrolysis sealing has been achieved. It sheds new light on the actual potential of metallic seals and constitutes a basis for ongoing studies, such as another French project, namely ANR/Pan-H/EMAIL.

Introduction

High-temperature electrolysis (HTE) is one of the most promising means to produce hydrogen. The CEA aims to achieve first electrolyser prototypes, for which water vapour production should not be responsible for CO_2 emission, by means of nuclear, geothermal and solar sources. To reduce hydrogen production costs, one way is to electrolyse water vapour at high temperature. The French project ANR/Pan-H/SEMIEHT contributes to this technological development, for which gas management and tightness achievement over a long period of time is a major challenge.

For the HTE process, the electrochemical cell consists of a tri-layer ceramic, well known for its brittleness, which limits applied loads. In addition, the relatively low ionic conduction properties of the electrolyte materials (3% yttrium-stabilised zirconia) requires an operating temperature above 700°C to reduce ohmic losses. This creates difficulties for the involved metallic materials, including bipolar plates and seals.

Two stack families exist: tubular and planar. The tubular architecture offers easier sealing solutions thanks to the bottom of the tube which constitutes in itself a tightness, but it has the disadvantage of high ohmic losses due to the length of electrical current lines. Planar geometries, used in the project SEMIEHT, offer more potential for high power but also require more complex sealing solutions. The major problem raised by these seals is that they have to run at high temperature between metals and ceramic materials. The latter have a lower thermal expansion coefficient and are brittle. Therefore, the tightness must be achieved with a relatively low load to protect the cell, the seal must be flexible enough to sustain the thermal expansion difference, and must also present a good creep resistance to ensure tightness over a long period of time. The maximum leak is fixed at about 1% of produced hydrogen, which corresponds to 10^{-3} Nml/min/mm on the GENHEPIS-G1 stack.

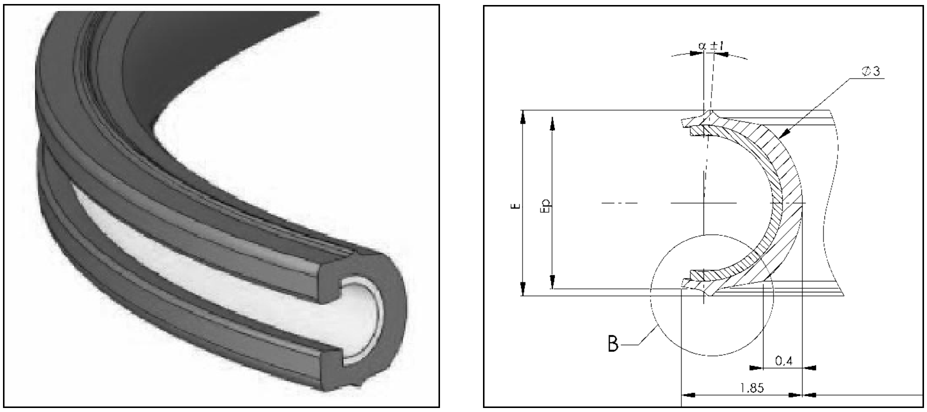
The typical sealing solution relies on glass-made seals, despite a large number of drawbacks. The glass materials are brittle below their transition temperature and may present cracks during cooling in particular because of expansion differences (Fergus, 2005). The glass-made seal also creates a rigid connection between the components of the stack, which can be responsible for critical stresses during thermal transients. With this type of non-metallic seal, the dismantling of components is difficult, indeed even impossible without changing the electrochemical cells. In addition, glass is likely to creep and does not sustain a pressure exceeding a few bars, possibly necessary in the near future for an industrial HTE stack. Finally, the glasses are not always chemically compatible with other components. They can lead to corrosion of bearing surfaces and can be responsible for Si pollution.

These drawbacks led to a search for alternative sealing solutions (Fergus, 2005; Lessing, 2007). Some results have been obtained by soldering the metallic interconnect to the ceramic cell (Weil, 2004). But the differences of thermal expansion make it very difficult in large dimensions because cooling after the solder solidification regularly causes rupture of the ceramic if no flexibility in the interconnect structure is introduced. Moreover, the HTE reducing atmosphere may damage the oxide solders. Other compressive seals based on mica (Chou, 2002) or simply metallic (Bram, 2007) are also studied. They require an external load to be controlled and maintained at high temperature to achieve an effective sealing. In addition, the seals involve metallic materials which should be oxidation resistant. The platinum and gold are excluded for obvious reasons of cost. The silver is being studied (Duquette, 2004), but seems to present problems in dual atmosphere (Singh, 2004), and vaporises. The Al_2O_3-forming alloys such as Fecralloy (Bram, 2001, 2004; Lefrançois, 2007) appear attractive for this application at high temperature. In addition, to establish the tightness with low load, the shape of the seal must favour local deformation in order to fill the interface roughness. Solutions are available industrially (Rouaud, 2002) and include a prominent seal structure in the contact area in order to localise stresses and strains. On one hand, the seal structure must be flexible enough to establish the tightness under low load, and to maintain it despite the expansion differences of the involved materials. On the other hand, the seal stiffness should be well chosen so as not to relax or creep during a long period at high temperature (Bram, 2002). Despite the price of manufacturing, the C shape appears to be a good candidate (Bram, 2001), although few results are available in temperature. Finally, the choice of temperature to establish tightening is crucial. Of course, it is easier to close the stack at room temperature. But, for the electrolysis process, sealing is only necessary during production, *i.e.* at the running temperature (~800°C). That is why, in a first approach, the tightening of the stack is achieved at high temperature and not at 20°C as already done by (Bram, 2004). This presents first, the advantage to allow the components to expand freely during heating and secondly, to facilitate the deformation of the seal which will have lower mechanical properties at high temperature.

A new seal design for the GENHEPIS prototype

Based on these thoughts, a new metallic seal is proposed. It presents a C shape section which is made of two components: an Inconel-X750-made inner part and a specially profiled Fecralloy-made "soft" outer lining. The seal is designed to be placed in a groove and to be submitted to a controlled displacement. At high temperature, this design can lead to relaxation by viscoplastic phenomena. In order to avoid too important load decrease, a strong inner part has been added. It is made of nickel-based superalloy and is supposed to stay in the elastic regime or at least not to creep in large proportions. The outer lining presents a prominent shape to be strained easily in order to be able to establish tightness under low load. This lining is made of Fecralloy (Fe-22%, Cr-5%, Al) and is first heat-treated at 900°C during 30 hours in order to form the protective alumina layer which also facilitates dismantling.

Figure 1: Details of the metallic seal



The GENHEPIS stack is presented in Figure 2 with three modules. The particularity of each module is to present a cell reinforcement made of stabilised zirconia. This thick piece has two major functions: the first one is to ensure the electric insulation between the two interconnects, and the other one is to transmit the load to tighten the seals without stressing the cell. The 3YSZ electrolyte of the cell is fixed to this support in order to form a tight barrier between the cathodic and the anodic chambers. This junction made of glass material is not detailed in this presentation. Moreover, the electric distribution is realised by specific small contacts made of ferritic stainless steel (Crofer, 22APU) to ensure flexibility. This stack presents two inlets (water vapour and air) and two outlets (hydrogen and oxygen). The anodic chamber is not tight and the oxygen is free to leak in the atmosphere. Tightness has to be ensured around the cathodic tubes in the anodic chamber and for the whole cathodic chamber. The new seal is used for these three junctions with different dimensions. Tightness around the inlet and outlet are achieved thanks to ϕ23 mm rings whereas the cathodic tightness is achieved thanks to a ϕ200 mm ring with the same cross-section. It can be observed that the small rings are deliberately positioned under the cell reinforcement and that the large one is placed above. A mass of 200 kg is used to close and tight the stack. Due to their dimensions, the small rings are compressed first. Therefore, this ensures that the cell is in contact with the inferior interconnect before the large ring and the small electrical contacts are loaded. This sequential loading is a real key to preserve the cell and seems to constitute an improvement for the stack architecture.

Experimental qualifications

Experimental procedure

The first part of the seal qualification tests is performed on a specific tightness test machine called "BAGHERA" at CEA Grenoble. It allows to study the relationship between the applied load, the seal

Figure 2: Details of the GENHEPIS stack

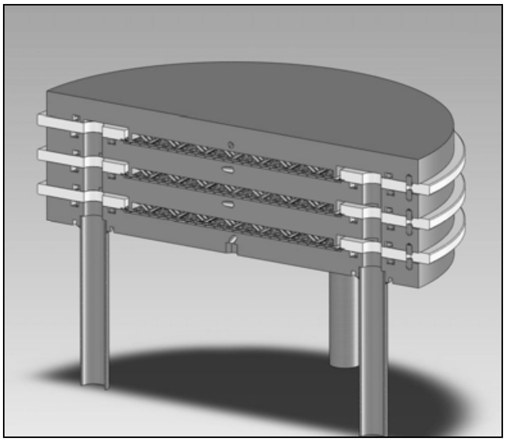
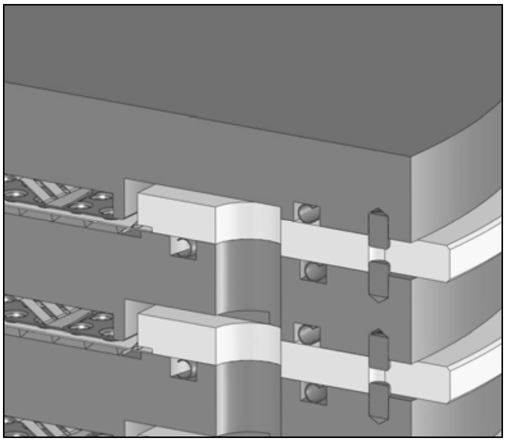
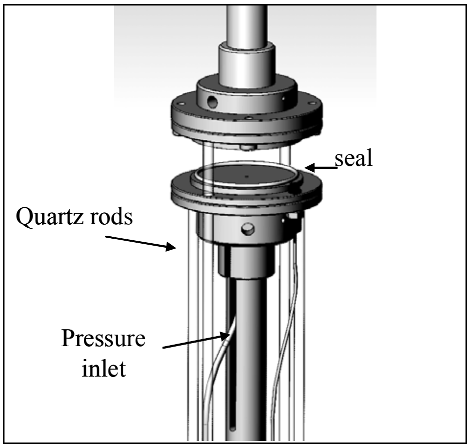


Figure 3: Details of the seal configurations



deformation and the leak at high temperature. It includes a 50 kN electromechanical testing device associated to a furnace to realise experiments up to 1 000°C in air. Specific tools, and in particular a displacement measurement system with quartz rods (Figure 4), have been developed to follow the seal compression as well as the leak flow. Concerning the presented tests, a MTS load cell of 5 kN has been used to tighten the seals. The leak measurement device has been developed to allow a relative pressure control between 1 and 1 000 mbar. Two different sensors are used. The measurement precision is equal to 0.1 mbar in the range 1-50 mbar and 1.5 mbar between 50 and 1 000 mbar. To follow the leak flow, two mass flow controllers from Brooks are used. Their range is 0.06-3 Nml/min and 2-100 Nml/min with an error equal to 0.7% of the measure plus 0.2% of the full scale. Three K-type thermocouples fixed on the bearing surfaces allow to record the temperature. The bearing surfaces are different on each side of the seal. The bottom one is metallic and made of nickel-based superalloy Udimet 720. It is machined by turning and presents a value of average roughness of Ra = 0.3. The upper one is made of 3% yttrium-stabilised zirconia and is made by tape casting. Once more, its roughness is around Ra = 0.3. The bearing surface materials have been chosen to introduce the effect of the thermal expansion difference on the leak flow. The tested seals are exactly the same as the small ones placed in the GENHEPIS stack. They have a diameter of 23 mm and have first been heat-treated at 900°C during 30 h to protect the outer lining and to facilitate the dismantling. The experimental procedure is as follows: the warming up to 800°C is realised without any loading. Then, the force is increased step by step to reach 3 N/mm. Finally, the last load level is maintained during the rest of the test, even during the cooling down. The leak flow is recorded during the whole test. For this study, the seals are tested with a relative pressure of 200 mbar.

Figure 4: Tightness test device



The second part of the seal qualification is performed in a HTE stack on the testing bench called "Tedhy" at CEA Grenoble. The experimental procedure is as follows: the warming up is done without loading, which allows the different pieces to expand freely. Then, a 200 kg mass is applied on the stack by 20 kg step every ten to twenty minutes. The total compression of the stack is followed by a displacement sensor, located outside the furnace, to be sure that each seal is completely in its groove. Finally, cermet reduction is performed and tightness is controlled before the electrolysis study begins. The input mass flow is a Brooks sensor with a range of 0.24-12 g/h and the outlet mass flow (Brooks) offers a range of 1.5-75 g/h. They have a precision of 0.7% of the measure plus 0.2% of the full scale. The tightness control is done with pure hydrogen by comparing the stack inlet flow and the stack outlet flow. Moreover, another way to check tightness is to measure humidity in both compartments. The hygrometers precision is 1.5%.

Experimental results

The analytical test performed on the seal with an imposed load is presented in Figures 5 and 6. It can be noted that the leak flow decreases continuously during loading. Under 3 N/mm, it reaches 0.005 Nml/min/mm corresponding to a loss of 5% of the produced hydrogen (based on GENHEPIS stack characteristics). During cooling, a strong increase of the leak, due to thermal contraction differences between bearing surfaces, is observed. Moreover, the chosen load level leads to a ring compressive displacement of 0.3 mm. This displacement increases by creep significantly up to 0.6 mm during the test. This is confirmed by the seal cross-section measured at the end of the test (Figure 7): the prominent part has completely disappeared, due to important local strains. Nevertheless, this contributes largely to a good tightness level if the creep is limited to this small prominent area. Other tests are still running to study the viscoplastic effects on the leak flow. More precisely, the load decrease during imposed displacement test is being quantified as well as its effect on the leak flow.

The tightness control for the stack is presented in Figure 8. It is performed with pure hydrogen just after the cermet reduction. The inlet and outlet mass flow signals are very similar. The difference is of +0.1 g/h at the outlet, keeping in mind a precision of 0.3 g/h. This means that before water injection, almost all the introduced hydrogen is collected. Moreover, the hygrometer at the anode outlet does not detect any water. This means that there is no leak between the two chambers.

Unfortunately, after 65 hours running, the test had to be stopped for other reasons. The metallic seals were dismantled without any difficulty.

Conclusions

Gas tightness over a long period of time is real challenge in high-temperature electrolysis. The presence of both metallic and ceramic materials is largely responsible for the difficulties. The thermal expansion differences and the use of brittle materials such as ceramics led to new sealing solutions. Here, a new metallic seal is proposed. It presents a C-shape with two components: a strong inner part, made of nickel-based superalloy X750 to avoid relaxation when the seal is compressed in its groove, and a specially profiled outer lining made of Fecralloy. Moreover, a stack design is proposed to tighten the seals at the operating temperature in order to let the stack pieces expand freely. Tightness qualifications on a specific device and during HTE stack tests are presented. These new metallic seal results are very encouraging for the future electrolysis stacks. They confirm that despite their stiffness, metallic steals can be used in stacks. This solution offer real potentials, such as robustness, pressure sustaining, and dismantling possibilities. Further investigations are realised in the French project ANR/Pan-H/EMAIL and should be published soon.

Figure 5: Leak measurement for each load level

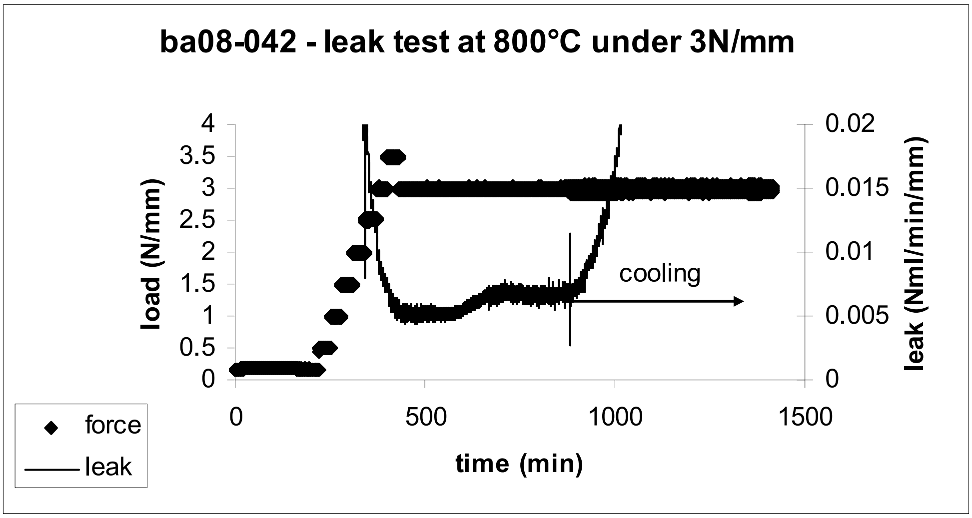


Figure 6: Displacement measurement for each load level

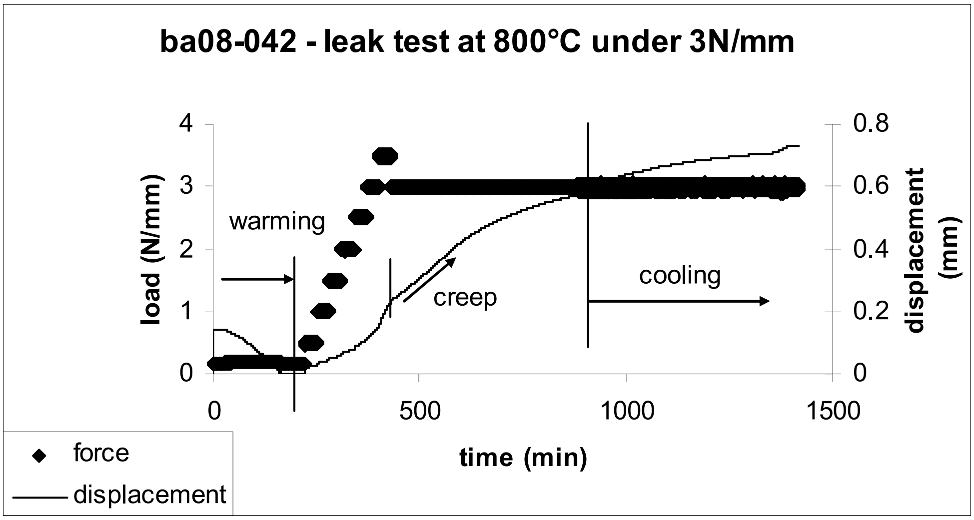


Figure 7: Cross-section of the tested seal

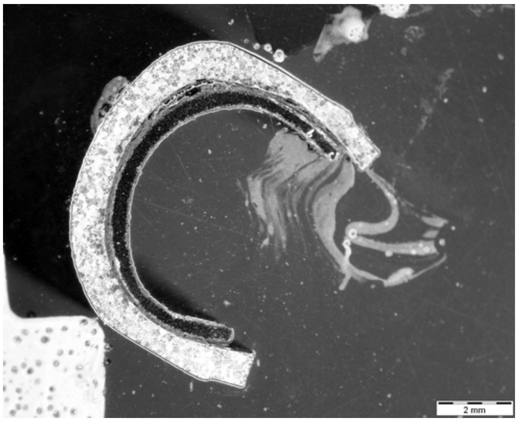
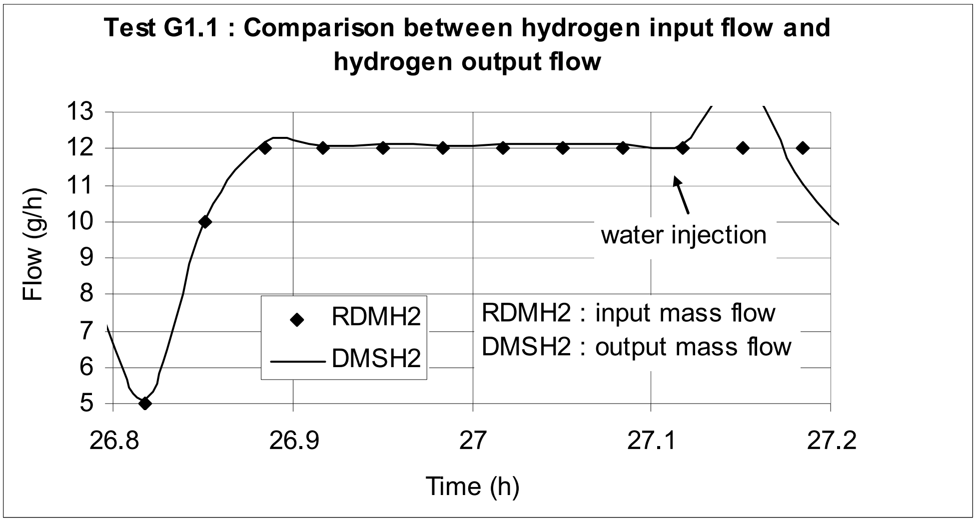


Figure 8: Leak control realised on stack with pure hydrogen just after cermet reduction



References

Bram, M., *et al.* (2001), *Electrochemical Society Proceedings*, Vol. 16, pp. 875-884.

Bram, M., *et al.* (2002), 5th *European SOFC Forum*, Lucerne, Switzerland, 1-5 July, Vol. 2, pp. 847-854.

Bram, M., *et al.* (2004), *Journal of Power Sources*, 138, pp. 111-119.

Chou, Y.S., *et al.* (2002), *Journal of Power Sources*, 112, pp. 376-383.

Duquette, J., *et al.* (2004), *Journal of Power Sources*, 137, pp. 71-75.

Fergus, J.W. (2005), *Journal of Power Sources*, 147, pp. 46-57.

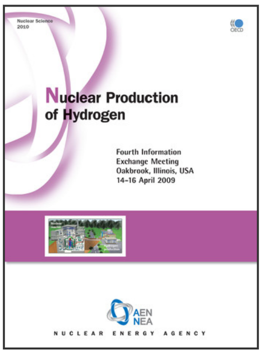
Lefrançois, M. (2007), *19th International Conference on Fluid Sealing*, Poitiers, France 25-26 September.

Lessing, A., (2007), *Journal of Materials Science*, 42, pp. 3465-3476.

Rouaud, C. (2002), WO 02 /086358.

Singh, P., *et al.* (2004), *Journal of Mat. Eng. and Performance*, Vol. 13 (3), pp. 287-294, June.

Weil, K.S., *et al.* (2004), *Fuel Cells Bulletin*, May, pp. 11-16.



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