Abstract

Tightness over a long period of time, in order to achieve an appropriate gas flow, 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 current sealing solution relies on glass-made seals, despite their low mechanical strength. 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 GENHEPI-S-G1 stack. Experiments were indeed 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. The metallic seals have been optimized throughout the project from an original Garlock design in order to decrease the seating load. They are also manufactured by Garlock. The C-shape 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 CO₂ emission, including 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 HTE process, the electrochemical cell consists of a tri-layer ceramics, well known for its brittleness, which limits applied loads. In addition, the relative 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 electrical current lines length. Plane geometries, used in the project SEMIEHT, offer more opportunities for high power but also 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 that have a lower thermal expansion coefficient and are brittle. Therefore, the tightness must be achieved with a relative low load to protect the cell, the seal must be flexible enough to sustain the expansion difference between the interconnectors and the cell, 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 current 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). Moreover, glass has to flow enough at running temperature to eliminate the cracks and to achieve tightness once more. The glass-made seal also creates a rigid connection between the components of the stack, which can be responsible of 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 few bars pressure, probably necessary in a close future for an industrial EHT stack. Finally, the glasses are not always chemically compatible with other components and can lead to corrosion of bearing surfaces.

These drawbacks lead to search for alternative sealing solutions (Fergus 2005) (Lessing 2007). Some results have been obtained by soldering the metallic interconnector 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. 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). The Al₂O₃ 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 encourage local deformation in order to fill the interface roughness. Solutions are available industrially (Caplain 2007) and include a prominent seal structure in the contact area in order to localize 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 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, ie at the running temperature (~ 800 °C). That is why the tightening of the stack can be achieved at high temperature and not only 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 base 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 deformed 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.

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 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 tongues made of ferritic stainless steel (Crofer 22APU) to ensure flexibility. This stack presents two inlets and one outlet (water vapour and hydrogen for the cathodic chamber and air for the anodic chamber). The anodic chamber is not tight and the oxygen is free to leak in the atmosphere. Tightness has to be realised around the cathodic tubes in the anodic chamber and for the whole cathodic chamber. The new seal is used for these three junctions with several dimensions. Tightness around the inlet and outlet are realised thanks to $\phi23$mm rings whereas the cathodic tightness is realised thanks to a $\phi200$mm ring with the same cross section. It can be observed that the small rings are deliberately placed under the cell reinforcement and that the large one is placed above. A mass of 200kg is used to close and tighten the stack. Due to their dimensions, the small rings are deformed first. Therefore, this insures that the cell is in contact with the inferior interconnect.
before the large ring and the small tongues 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 realised on a specific tightness test machine called “BAGHERA” at CEA Grenoble. It offers to study the relationship between the applied load, the seal deformation and the leak at high temperature. It includes a 50 kN electromechanical testing device associated to a furnace to realise tests up to 1000°C in air atmosphere. Specific tools, and more particularly 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 5kN has been used to tight the seals. The leak measurement device has been developed to allow a relative pressure control between 1 and 1000 mbar. For this study, the seals are tested with a relative pressure of 200mbar. Two different sensors are used. The measurement precision is equal to 0.1 mbar in the range 1-50 mbar and 1.5mbar between 50 and 1000 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 inferior one is metallic and made of Udimet 720 Nickel base superalloy. It is machined by turning and presents a roughness of Ra=0.3. The superior one consists in an electrolyte made of 3% yttrium stabilised zirconia and is realised by tape casting. Once more, its roughness is around Ra=0.3. The bearing surface materials have been chosen to introduce an expansion coefficient difference in order to also study its effects on the leak flow. The tested seals are exactly the same as the small ones
placed in the Genhepis stack. They present a diameter of 23mm and have been first heat treated at 900°C during 30h 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 3N/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.

The second part of the seal qualification is realised in the stack on the testing bench called “Tedhy” at CEA Grenoble. The experimental procedure is as follows: The warming up is realised without loading, which allows the different pieces to expand freely. Then, a 200kg mass is applied on the stack by increasing the load of 20kg every ten to twenty minutes. The total compression of the stack is followed by a displacement sensor, placed outside the furnace, to be sure that each seal is completely in its groove. Finally, the cermant reduction is realised and the tightness is controlled before the electrolysis study begins. The input mass flow is a Brooks sensor with a range of 0.24-12g/h and the outlet mass flow (Brooks) offers a range of 1.5-75g/h. They have a precision of 0.7% of the measure plus 0.2% of the full scale. The tightness control is done by comparing the hydrogen inlet flow and the hydrogen outlet flow just at the end of the cermant reduction (with pure hydrogen). Moreover, hygrometers are used to follow the cermant reduction, and to detect a leak between cathode and anode. Its precision is 1.5%.

**Experimental results**

The analytical test realised on the seal with an imposed load is presented in Figure 5 and in Figure 6. It can be noticed that the leak flow decreases continuously during loading. Under 3N/mm, it reaches 0.005 Nml/min/mm corresponding to a loss of 5% of the produced Hydrogen on Genhepis stack. During cooling, a strong increase of the leak, due to the contraction differences between bearing surfaces, is observed. Moreover, the chosen load level leads to a ring displacement of 0.3 mm. This displacement increases by creep significantly up to 0.6mm during the test. This is confirmed by the seal cross section realised 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 decreasing 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 realised with pure hydrogen just after the cermet reduction. The inlet and outlet mass flow signals are very similar. The difference is of +0.1g/h at the outlet, keeping in mind a precision of 0.3g/h. It 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, a leak is detected. The glass junction between the cell and its support has flowed out. The metallic seals can be dismantled without any difficulty.

![Test G1.1: Comparison between hydrogen input flow and hydrogen output flow](image)

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

**Conclusions**

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

**References**