High Temperature Steam Electrolysis stack with enhanced performance and durability

Julie Mougin*, A. Chatroux, K. Couturier, M. Petitjean, M. Reytier, G. Gousseau, F. Lefebvre-Joud

CEA/LITEN, 17 rue des Martyrs, F-38054 GRENOBLE Cedex 9, France

Abstract

High Temperature Steam Electrolysis (HTSE) is one of the most promising ways for hydrogen production. If coupled to a CO₂-free electricity and low cost heat sources, this process is liable to a high efficiency. The present study describes recent promising results obtained in terms of performance and durability in stack environment, thanks to the use of protective coatings on one hand, and of advanced cells on the other hand. As for Solid Oxide Fuel Cells, it has been demonstrated that the integration of protective coatings was mandatory to decrease the degradation rate in HTSE stacks, and that with optimized coatings, (CoMn)₂O₄ in the present case, the same durability as the one of the single cell tested in a ceramic housing could be reached. The type of cell was also shown to play a major role on the degradation rate. With advanced cells, degradations below 2%/kh could be reached. The higher is the current density, the higher is the degradation rate, with a mostly reversible effect. These degradation rates are close to the objectives, even if a bit higher than in SOFC mode. Finally a low-weight stack has been designed, targeting high performance and durability while reducing the cost by the use of thin interconnects. An electrochemical performance similar to the previous stack design has been obtained for a 3-cell stack (-1 A/cm² at 1.3 V at 800°C), with degradation rates below 3%/1000h in the testing conditions. The thermal cyclability of stacks has been demonstrated, from 800°C to 20°C, as well as electrical load cycling. The results showed that the HTSE stacks considered in the present study can cycle very rapidly, and that the cycles considered do not induce any degradation. Therefore it can be concluded that these results makes HTSE technology getting closer to the objectives of performance, durability, thermal and electrical cyclability and cost, and that HTSE is a candidate to produce hydrogen as a mean to store renewable intermittent energies.

© 2012 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of Canadian Hydrogen and Fuel Cell Association. Open access under CC BY-NC-ND license.

Keywords: High Temperature Steam Electrolysis, stack, performance, durability

* Corresponding author. Tel.: +33.4.38.78.10.07; fax: +33.4.38.78.41.39. E-mail address: julie.mougin@cea.fr.
1. Introduction

High Temperature Steam Electrolysis (HTSE), based on reversed solid oxide fuel cell technology, appears as a relevant process to produce CO\textsubscript{2}-free hydrogen and oxygen.

The dissociation of steam into \textit{H}_2 and \textit{O}_2 requires less energy than in the case of the electrolysis of liquid water. In addition, when the temperature increases, a part of the energy required for the steam dissociation can be brought by heat instead of only electricity. It can be high temperature waste heat and surplus energy from power plants during off-peak hours [1]. These elements make the HTSE technology promising in terms of global efficiency. The highest could be the temperature, the best would be the efficiency, all the more that electrochemical kinetics are favored by the increase of the temperature. However, limitations due to materials and costs occur and the targeted operating temperature is around 800°C or even below, down to 700°C. To become competitive with other hydrogen technologies, HTSE has to exhibit high durability (25000 hours) and high performances (high hydrogen production rates, i.e. \textasciitilde40 mgH\textsubscript{2}/cm\textsuperscript{2}/h or \textasciitilde1 A/cm\textsuperscript{2} but also good gas tightness to recover as much as possible the hydrogen produced). In addition, cost-effective stack and system components have to be considered.

The strategy adopted to fulfill all the requirements of performance, durability and cost given above is a strategy of piece by piece validation. First a stack design has been proposed to validate that the performance targeted could be reached, with at this stage no cost-efficiency consideration since thick interconnect plates were considered. Special attention has been paid to the most critical components (i.e. contact coatings and sealing). Indeed, any contact resistance would limit hydrogen production and any leakage would decrease the \textit{H}_2 and \textit{O}_2 production efficiency. It has been shown it is possible to reach the performance target of \textasciitilde1 A/cm\textsuperscript{2} at 1.3 V at 800°C at the stack level [2-3]. This 5-cell stack has then been tested for a long term durability test of 3000 h, the gas-tightness being maintained during the whole duration of the test, proving the robustness of this design. However, the degradation rate obtained was around 8%/1000h, without any protective coatings on the interconnects [2-3]. Thus actions have been carried out to improve the durability, mainly by integrated protective coatings. The positive effect of such coatings has been proven and is presented in the present study.

From these results, this stack design has then been considered as a reference, highly performing and robust stack, for which reproducibility has been proven several times. It is perfectly suitable to integrate and validate new components like other coatings, new sealing concepts and advanced cells, both in terms of performance and durability. In the present study, the positive effect of the integration of advanced cells on the performance and durability is presented.

Then attempts have been made to optimize the cost of the stack, without decreasing the performance and the durability. A low-weight stack has thus been designed, taking advantage of the achievements previously obtained on the robust stack. The corresponding results are reported in this paper.

Finally the questions of cyclability, both in terms of thermal cycling and electrical load cycling, have been considered and studied. Some results are presented here. Indeed, even if HTSE does not target often stop and start cycles, several complete thermal cycles have to be done over its lifetime at least for the maintenance operations. In addition, in case HTSE is considered to produce hydrogen as a mean to store renewable intermittent energies, electrical load cycling has to be considered.

2. Experiments
2.1. Description of stack designs and components

The reference high performance and robust stack was presented elsewhere [2-3]. For the present studies, the 150x150 mm interconnects made of 10 mm thick Crofer® 22 APU plates were coated by a (Co,Mn)$_3$O$_4$ spinel protective coating on the oxygen side, deposited by magnetron sputtering [4]. Nickel grids were considered as contact layers on the hydrogen side, whereas a screen printed LSM contact layer was applied on top of the spinel protective coating on the oxygen side. Sealing was achieved through a square frame with insulator and ceramic glass Schott G018-304. A mica foil was added between each interconnect plate for electrical insulation.

The cells were 120x120 mm with an active area of 100 cm². Several types of cells were considered:

- First a reference commercial electrode supported cell, with a NiO/YSZ cermet (thickness ~ 500 µm), a 5 µm thick 8YSZ electrolyte, and a YDC-LSCF oxygen electrode (~ 45 µm thick).
- Second an advanced electrolyte supported cell provided by ECN, with a 90 µm thick 3YSZ electrolyte, a hydrogen electrode made of GDC(Co)-NiO/GDC-NiO (~ 55 µm thick) and an oxygen electrode made of YDC-LSCF (~ 70 µm thick)
- Finally an advanced electrode supported cell, designed for low temperature operation and provided by ECN, with a NiO/YSZ cermet (thickness ~ 500 µm), a 5 µm thick 8YSZ electrolyte, and a GDC-LSC oxygen electrode (~ 20 µm thick).

Results obtained at the SRU level are presented here and compared to the ones previously obtained at the 5-cell stack level (for stack results see more details in [2-3]).

The low-weight and thus more cost-efficient stack design also considers Crofer® 22 APU –based interconnects, the thickness of each interconnect being decreased to 0.6 mm. The sealing solution as well as the contact coatings are derived from the one developed for the robust stack presented above. For the test results presented in this paper, no protective coatings were applied. Reference commercial electrode supported cells as described above were considered. Results obtained at the scale of a 3-cell stack are presented.

2.2. Test procedure and operating conditions

The testing protocol comprises a first stage aiming at reducing the hydrogen electrode, at applying adapted mechanical load and at checking the quality of the stack in terms of electrical contact and gas tightness within the stack. It is followed by a second stage in the electrolysis mode at 800°C by increasing steam partial pressure to 90 vol%, balanced by hydrogen to reduce the risk of cermet re-oxidation at Open Circuit Voltage (OCV). The steam flow rate is controlled thanks to a liquid water mass flow controller (delivered by Brooks Instrument) coupled with a home-made steam generator. During this step, total flow rates and type of sweeping gas in the anodic compartment are optimized. The SRU/stack performances are characterised by i-V curves. The current density obtained at the thermoneutral voltage of 1.3 V is taken to evaluate the performance of the SRU/stack. Negative current densities define operation in HTSE mode.

Voltage probes are used to record the voltage of each cell in the case of stack tests, and K-type thermocouples are placed in the SRUs or stacks to monitor the temperature.

In order to evaluate the gas tightness, a measurement of the flow rates exhausted from the SRU/stack is done thanks to mass flow rate meters at the outlet of each compartment, after condensation of the unused water.
For thermal cycles, complete cycles were considered, from 800°C down to 20°C and then up again to 800°C. During the thermal transients the atmospheres were nitrogen+3%H₂ on H₂ side and air on O₂ side. The cooling and heating rates were set to 1 °C/min. For the cooling step, and particularly for low temperatures, the furnace inertia decreased the cooling rate.

For electrical cycles, two types of electrical loads have been considered:
- a first very rapid cycling, from i=0 A/cm² (corresponding to the OCV) up to a current density corresponding to the thermoneutral voltage 1.3 V (around –1 A/cm²), with plateau of 10 s at OCV and at 1.3 V. In this case only an electric cycling is applied since the cycles are too rapid to allow any thermal or gas composition effects
- a second slower cycling, from i=0 A/cm² (corresponding to the OCV) up to a current density corresponding to the thermoneutral voltage 1.3 V (around –1 A/cm²), with plateau of 10 min at OCV and at 1.3 V. In this case thermal and gas composition effects have time to be superimposed to the electrical effects.

![Fig. 1. Representation of (a) the fast electrical load cycle and (b) slow electrical load cycle from the OCV to the thermoneutral voltage of 1.3 V (rigorously 1.28 V at 800°C)](image)

3. Results

3.1. Effect of the protective coatings

The effect of the (Co,Mn)₃O₄ spinel protective coating on the oxygen side of the interconnect has been checked at the SRU level with a reference commercial cell. Figure 2(a) presents the durability curve of such a SRU compared to durability curve obtained for the 3 central cells of the 5-cell short stack, tested in the same conditions but without coating [2-3].

![Fig. 2. Durability curve obtained for a SRU containing a (Co,Mn)₃O₄ spinel protective coating on the O₂ side of the interconnect and a reference commercial cell, and comparison (a) to the curves of the 3 central cells of a 5-cell short stack without coating (see [2] for more details); (b) to the curve of a single cell tested in a ceramic housing; tests performed at 800°C, in 90%H₂O/10%H₂ on the hydrogen side, air on the oxygen side, i = -0.5 A/cm², corresponding steam conversion rate SC=25%](image)
The presence of the protective coating is found to decrease the degradation rate down to 6%/1000h, whereas it was between 7 and 13%/1000h in stabilised regime on the 3 central cells of the stack without coating (Fig. 2(a)).

However, it is worth noticing that the same type of cell tested in a ceramic housing presents a similar durability curve, highlighting that most of the remaining degradation is due to the cell (Fig. 2(b)). These results fully validate the efficiency of such a protective coating, at least for the duration and the test conditions considered.

3.2. Effect of the implementation of advanced cells

Thus in order to decrease further the degradation rate to get closer to the specifications, advanced electrolyte and electrode supported cells have been implemented at the SRU level, the SRU containing a (Co,Mn)₃O₄ spinel protective coating and the contact coatings previously validated.

Figure 3(a) presents the i-V curve, whereas durability curves at various current densities are presented in Figure 3(b) for the advanced electrolyte supported cell. A current density of -0.6 A/cm² at 1.3 V can be obtained for such a cell at 800°C, which is a very good performance for an electrolyte supported cell. Degradation rates between 1.6 and 2.7 %/1000h are obtained with such a cell which is much lower than the values reported above for the reference commercial electrode supported cell. The degradation rate is found to increase with the current density (Fig. 3(b)), but looks mostly reversible since the last step carried out at -0.4 A/cm² leads more or less to the same degradation rate as the 1st step carried out in the same conditions. It is worth noticing that the step at high current, which corresponds to an operation in strong exothermal mode, does not lead to an acceleration of the degradation, since the dependency of the degradation rate with the current density looks almost linear.

Similarly Figure 4 presents the i-V curve and the durability curve obtained at 700°C for a SRU integrating the advanced electrode supported cell. A current density of -1.1 A/cm² at 1.3 V can be obtained for such a cell at 700°C, which is as good, even slightly better than the performance obtained for the reference commercial cell tested at 800°C in the same SRU. This confirms the high potential of such a
cell for operation at low temperature, around 700°C or even lower. A degradation rate around 1.8 %/1000h is obtained for a current density of -0.5 A/cm², which is similar to what was obtained with the electrolyte supported cell, and much better (factor 3) than the value obtained with the reference commercial electrode supported cell. The 100°C of temperature decrease could help in slowing down the degradation mechanisms. As previously mentioned for the other type of cell, the increase of current density increases the degradation rate, and this effect is mostly reversible. It is worth noticing that the advanced electrode supported cell leads to a degradation rate similar to the one of the reference commercial cell, but for a current density twice higher. This value is higher than the one reported by Schefold et al., which was 3.8 %/1000h at –1 A/cm² [5], but for a single cell and for a lower SC ratio, equal to 36%, whereas it is 64% for the same current density in the present case. The scale of test, SRU versus single cell as well as the SC ratio, which is found to play a role on the cell degradation [6], could explain this difference.

Results obtained on both types of advanced cells show it is possible to decrease the degradation rate down to 1.6-1.8 %/1000h, either by using optimised electrolyte supported cells or by lowering the operating temperature down to 700°C for electrode supported cells. It also seems necessary, for the testing conditions of the present study, to apply a current density below –1 A/cm² and intermediate steam conversion rates to keep a moderate degradation rate. However, it is worth noticing that the degradation rates always remain higher than those reported in SOFC mode.

3.3. Performance and durability of the low-weight stack

The possibility to achieve high performances and low degradation rates being proven in the previous sections, the performance and durability of the low weight stack targeting a low cost are presented in Figure 5 for a 3-cell stack tested at 800°C with reference commercial cells.

A performance of –1 A/cm² is achieved for a voltage of 1.20-1.33 V (Fig 5(a)), which fully validates the design of the low-weight stack, since this performance is similar to the one of the robust thick stack and the single cell tested in a ceramic housing (see [2] for comparison). The degradation rate in steady state operation (e.g. after 400h) is found between 2.1 and 2.7%/1000h for the 3 cells, without any protective coating on the interconnects. These values are rather low, and close to values reported above for advanced cells. These values could look surprisingly low since reference commercial electrode supported cells were considered, which presented higher degradation rates in above section (Fig. 2). It is worth noticing that a new batch of cells was considered to manufacture this stack, which could explain at
least partly this difference. These values are lower than those reported by Brisse et al. for a 5-cell stack tested at 820°C at -0.4 A/cm² and a SC of 40%, which led to a degradation of 5.6 %/1000h [7]. The difference in testing conditions makes the direct comparison difficult. Nevertheless, such moderate degradation rates make this low-weight stack very promising in terms of performance as well as in terms of durability, since the performance target is achieved, the degradation rate is close to the targets, and the cost is strongly reduced.

### 3.4. Thermal and electrical load cycling

Both robust SRU and low-weight 3-cell stack have been submitted to complete thermal cycles from 800°C down to 20°C and back to 800°C. Figure 6 presents the results of 3 of such cycles on the robust SRU integrating reference commercial cells in terms of gas tightness, measured in nitrogen +3 %H₂ during the thermal cycles for safety reasons, and electrochemical performances (Figs. 6(a) and 6(b) respectively).

It is found that the gas tightness is maintained over the whole duration of the thermal cycles, even at low temperature. The 3 thermal cycles do not impact the performance of the SRU since no evolution of
the i-V curves is observed. These results fully validate the sealing solution developed, at least for few cycles in the considered conditions.

Figure 7 presents the i-V curves obtained after one complete thermal cycle on the low-weight stack. It is found that the low-weight stack is also able to sustain one thermal cycle. Tests are planned to investigate its behaviour upon several thermal cycles.

Figure 8 presents the effect of fast and slow electrical load cycling from the OCV to a current density corresponding to the thermoneutral voltage. It is first noticed that the SRU is able to follow very fast electrical load transients. Both types of cycles do not affect the durability. It shows that HTSE can be appropriate for following the electrical load profile of renewable intermittent energy sources, at least for the cycles considered.

4. Conclusions
Former studies have highlighted it was possible to reach a performance as high as – 1 A/cm² at 1.3V, which was demonstrated through a high performance and robust stack design integrating reference commercial cells, but the degradation rates, around 8%/1000h were too high. It has been proven that the implementation of a (CoMn)₃O₄ protective coating on the oxygen side interconnect allowed decreasing the degradation rate to around 6%/1000h. It has been demonstrated that this value was similar to the one measured on a single cell tested in a ceramic housing, proving the efficiency of such a protective coating. The degradation rate was however still too high. Thanks to the use of advanced electrolyte or electrode supported cells, degradation rates below 2%/1000h have been obtained at the SRU level, which is much closer to the objective, even if a bit higher than in SOFC mode. It has been found that higher current densities led to higher degradation rates, but that it was mostly reversible.

Three complete thermal cycles have been successfully performed for such a design at the SRU level, with no loss of the gas tightness during the thermal transients and with similar electrochemical performances after each thermal cycle. These results validate the sealing solution and evidence the robustness of the stack design. Two types of electrical load cycles have also been performed, either slow or fast, from the OCV to the thermoneutral voltage of 1.3 V. The results showed that the HTSE stack can cycle very rapidly, and that the cycles considered do not induce any degradation. This makes HTSE a candidate to produce hydrogen as a mean to store renewable intermittent energies.

Finally a low-weight stack has been designed, keeping the advantages of the high performing and robust stack previously validated in terms of performance, durability and cyclability, but aiming at reducing the cost by the use of thin interconnects. An electrochemical performance as high as the one of the robust stack has been obtained, with degradation rates below 3%/1000h for a 3-cell stack. The thermal cyclability of this stack has also been demonstrated with one thermal cycle. Therefore it can be concluded that these results makes HTSE technology getting closer to the objectives of performance, durability, cyclability and cost.

Acknowledgements

This work has been partly supported by French Research National Agency (ANR) through Hydrogen and Fuel Cells program (FIDELHYO project n°ANR-09-HPAC-005-01) and by the European Commission (RELHY project, grant agreement 213009, and ADEL project, grant agreement 256755). The authors would also like to acknowledge additional industrial support. Finally colleagues from CEA, Philippe Szynal, Michel Planque, Bruno Oresic, Stéphane Di Iorio, Aude Brevet and Aurore Mansuy are greatly thanked for their participation to this work. Bert Rietveld and colleagues from ECN are also acknowledged for their fruitful collaboration.

References

