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C2FUEL

Carbon Captured Fuel and Energy Carriers for an Intensified Steel Off-Gases based Electricity Generation in a Smarter Industrial Ecosystem

Deliverable

D2.2– Influence of operation conditions on single cells performance and durability

WP2 – High temperature electrolysis development

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Deliverable report

1 Executive Summary

1.1 Description of the deliverable content and purpose

In this deliverable, the influence of operation conditions such as temperature, gas cleaning, steam utilization, current density and oxygen electrode sweep gas on solid oxide single cells performance and durability will be reported. The cells were tested under different conditions in order to map out the suitable electrolysis operation window for [**ELCOGEN**] cells and possibly to provide optimal operation parameters input for the SOEC demonstration unit operation.

1.2 Brief description of the state of the art and the innovation breakthroughs

State of the art fuel electrode supported solid oxide electrolysis cell consist of a 400 µm thick Ni-YSZ fuel electrode support and 12-18 µm Ni-YSZ fuel electrode active layer; a ca.2 µm YSZ electrolyte, a ca. 2 um CGO barrier layer and LSC oxygen electrode were used; the effect of different operation parameters on the durability of the cells were reported. Detailed electrochemical analysis were carried out to identify the courses of the degradation under different operation conditions.

1.3 Corrective action (if relevant)

Not applicable.

1.4 IPR issues (if relevant)

Not applicable

2 Introduction

The first object of C2fuel project is to develop a high temperature electrolysis demonstration unit producing 1 Nm^3/h hydrogen at 40 bar level to be operated in an industrial-relevant environment. In order to facilitate this, SOE cells will be investigated with respect to their electrochemical performance and durability for both steam electrolysis, co-electrolysis and CO_2 electrolysis. The influence of different operation parameters, such as temperature, current density, inlet gas composition, steam utilization etc. were studied in order to better understand the performance of [ELCOGEN] cells under electrolysis operation conditions and identify which parts of the cell limits the lifetime. The results are to be further explored to provide testing guidelines for stack and demonstration unit operation in this project.

3 SOEC initial performance under different test conditions

Figure 1 presents the initial current-voltage (iV) performances of the SOEC cell under different temperature and inlet gas compositions. The total flow of the inlet gas was kept the same as 13.4 L/h during the iV characterization and on the oxygen electrode compartment, a 100 L/h of Air was supplied. Three inlet gas compositions were tested, 10%H_2 + 90%H_2O for steam electrolysis, 10%H_2 + 45%H_2O + 45%CO_2 for co-electrolysis and 10%CO + 45%CO_2 for CO_2 electrolysis. For the co-electrolysis and CO_2 electrolysis tests, the maximum current density was limited to 0.75A/cm^2 in order to avoid carbon formation at high fuel utilization and low temperatures. In general, the cell shows very good performances thanks to its thin electrolyte. The calculated tangent area specific resistances from the iV curves are presented in Table 1. As expected, the cell performance increases with the increasing of temperature due to faster kinetics and lower resistance, but decreases with the increasing of CO_2 concentration due to the slower kinetics of CO_2 electrolysis. The specific energy consumption calculated from the iV data at 700°C, -0.5A/cm^2 is 2.3, 2.32 and 2.41 KWh/m^3 for H_2 production, H_2+CO production and CO_2 production respectively.

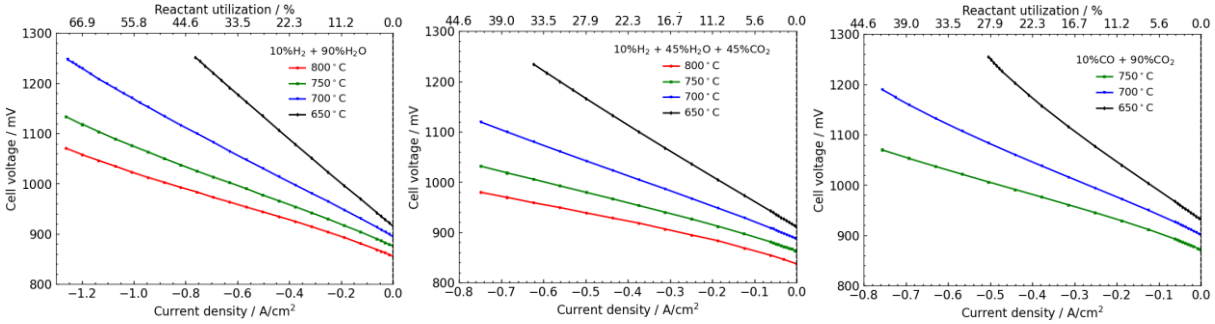


Figure 1 : Cell performance under different temperatures and gas compositions.

Table 1: Tangent Area specific resistance calculated at 0.25 A/cm2 from the iV curves

	ASR at 0.25A/cm², Ω·cm²		
Fuel electrode inlet gas / Temperature	10%H_2 + 90%H_2O	10%H_2 + 45%H_2O + 45%CO_2	10%H_2 + 90%CO_2
800°C	0.171	0.189	-
750°C	0.195	0.216	0.246
700°C	0.252	0.305	0.345
650°C	0.443	0.508	0.62

4 Durability of SOEC tested under different test conditions

4.1 Effect of temperature

The study of the effect of temperature on the durability of the cells has been realized by testing the cells at the same condition but different temperatures. The durability tests were carried out at 750, 700 and 650°C respectively, under -0.5 A/cm² with 13.4 L/h 10% H_2 + 90% H_2O supplied to the fuel electrode compartment and 100 L/h air supplied to the oxygen electrode compartment. The theoretical steam utilization calculated by faraday law is 56%. Cell voltages were recorded during the durability tests and are presented in Figure 2. It is worth to note that the test performed at 750 °C was carried out without passing the inlet H_2 through the gas cleaning filter. The overall and the last 200 hours degradation rates for the cells operated at three operation temperatures were calculated and presented in Table 2. It can be seen that temperature plays a very important role in the cell degradation. The higher the temperature, the lower the degradation rate. The cells operated at 750 and 700 °C show similar degradation behavior, firstly with a slow degradation rate in the first 300 hours, followed by a accelerate degradation rate in the 300-600 hours then reach the long-term degradation after 600 hours. In the last 200 hours, both cells showed very similar degradation rates of ca. 100mV/1000h. However, the cell operated at 650°C exhibits faster degradation both initially and in the last 200 hours. The results indicate that the temperature has a strong effect on the cells durability; higher operation temperature can reduce the degradation rate.

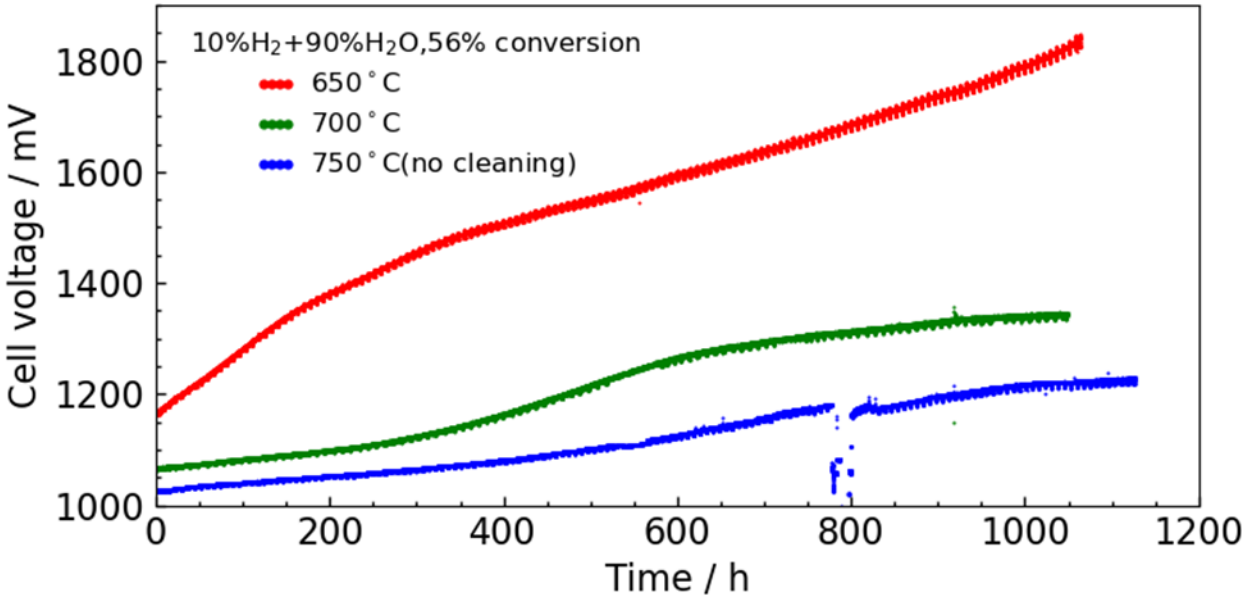


Figure 2: Cell voltage as a function of operation time for the tests performed at 750, 700 and 650°C under -0.5 A/cm2 with 10% H2 + 90% H2O supplied to the fuel electrode and Air supplied to the oxygen electrode.

Table 2: Overall degradation rates and last 200h degradation rates

Calculated degradation rates	Temperature		
	650	700	750
Overall, mV/kh	633	264	174
Last 200h, mV/kh	603	109	104

Electrochemical impedance spectra (EIS) were recorded during the durability tests. The serial resistance Rs, polarization resistance, Rp and area specific resistance, ASR extracted from the impedance spectra data are plotted in Figure 3. It can be seen that cells tested at 700 and 750 °C started with very similar Rs and Rp values, but a higher Rs and Rp is observed on the cell operated at 650 °C. Cell tested at 750 °C exhibited the lowest Rs increase during the durability operation, while cell tested at 650 °C showed the highest Rs increase. As can be also seen from Table 3 , the calculated degradation rates for Rs, Rp and ASR, the overall ASR degradation rates are similar for the cells tested at 700 and 750 °C. The cell tested at 650 °C exhibits more than twice higher ASR degradation rate than the two higher temperature test cells.

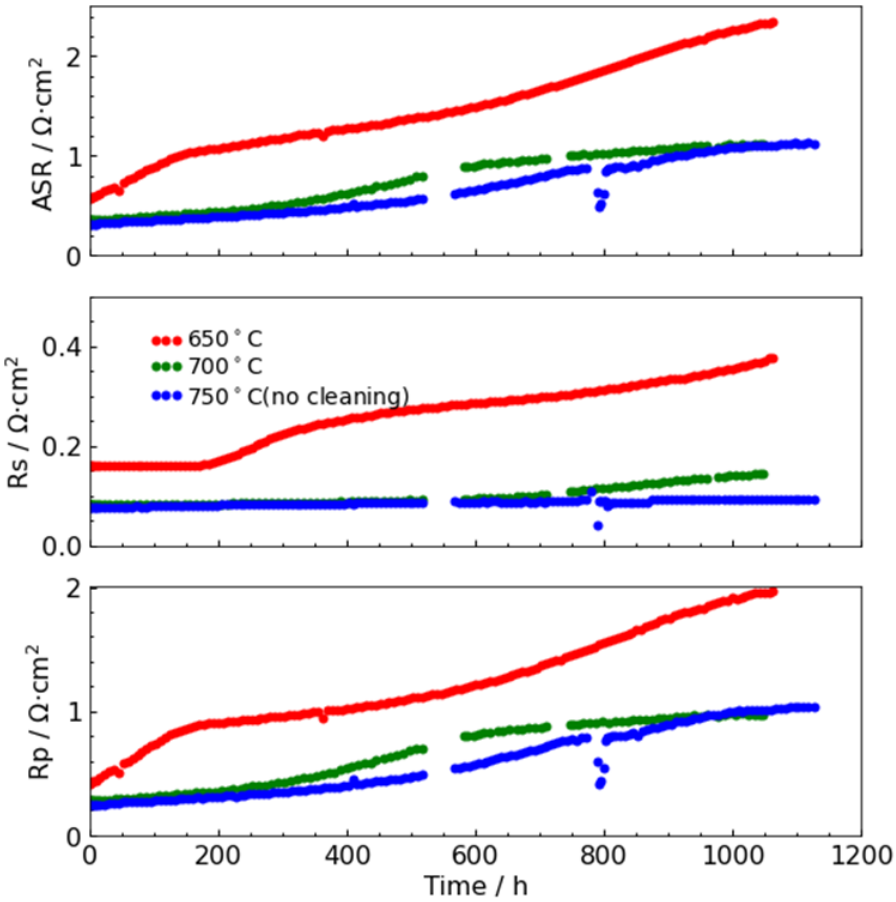


Figure 3: Serial resistance Rs, polarization resistance and area specific resistance extracted from the impedance spectra measured during the durability operation for the three temperatures tested cells.

Table 3: Rs, Rp and ASR extracted from the impedance spectra measured during the durability operation of the three temperature operated cells

Resistance Degradation Ω.cm²/kh	Temperature		
	650	700	750
Rs	0.2	0.06	0.02
Rp	1.46	0.66	0.7
ASR	1.66	0.72	0.72

To further identify the cause of the degradation, electrochemical impedance spectra (EIS) measured during the durability tests were analyzed by using the distribution of relaxation time (DRT) method. The EIS and DRT results are presented in Figure 4. It can be seen that the change of the impedance decreases with the increasing of temperature. From DRT analysis, the main DRT peak change takes place at characteristic frequency arrange of 10-1kHz with a summit frequency at ca. 200 Hz which can be mainly attributed to the fuel electrode process, which indicated that fuel electrode is responsible for the main degradation However, it is worth to mention that the changing of oxygen electrode process, typically at frequency range of 30-80 Hz for such type of cells, was

overlapped with the fuel electrode process, which makes it difficult to separate the oxygen electrode contribution from the overall degradation, even though it is known that the contribution of the oxygen electrode is rather small. Nevertheless, for the cell operated at lower temperature at 650°C, a noticeable peak at frequency around 30 Hz can be observed, which might be originated from the oxygen electrode process, indicating that the lowering of the operation temperature also led to the degradation of the oxygen electrode. Operating the cell at higher temperature apparently can reduce the cell degradation.

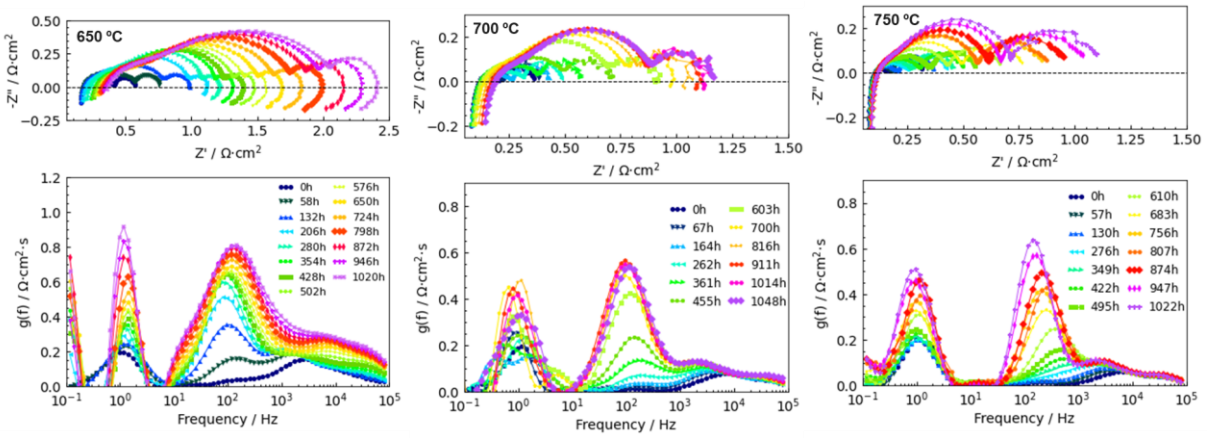


Figure 4: EIS and DRT analysis of the impedance measured during the durability test of the three cells operated at 750, 700 and 650°C respectively.

4.2 Effect of gas cleaning

One of the main causes for SOEC degradation is due to the impurities such as sulphur or silica species from the inlet gas stream that can poison the Ni electro-catalyst in the fuel electrode. In order to eliminate such impurities, fuel gas stream was cleaned by using a gas cleaning filter filled with commercial gas clean powders. Two tests with and without gas cleaning filter were performed to study the effect of gas cleaning. Durability tests were performed at 700 °C with 10% H_2 + 90% H_2O supplied to the fuel electrode and air supplied to the oxygen electrode. The cell voltages development for both tested cells with or without gas cleaning are presented in Figure 5. The cell tested without gas cleaning exhibits a fast initial degradation then a linear long-term degradation, while degradation of the cell with gas cleaning showed a tendency to level off after the initial degradation. The overall and last 200 hours degradation rates calculated from the voltage data are presented in Table 4.

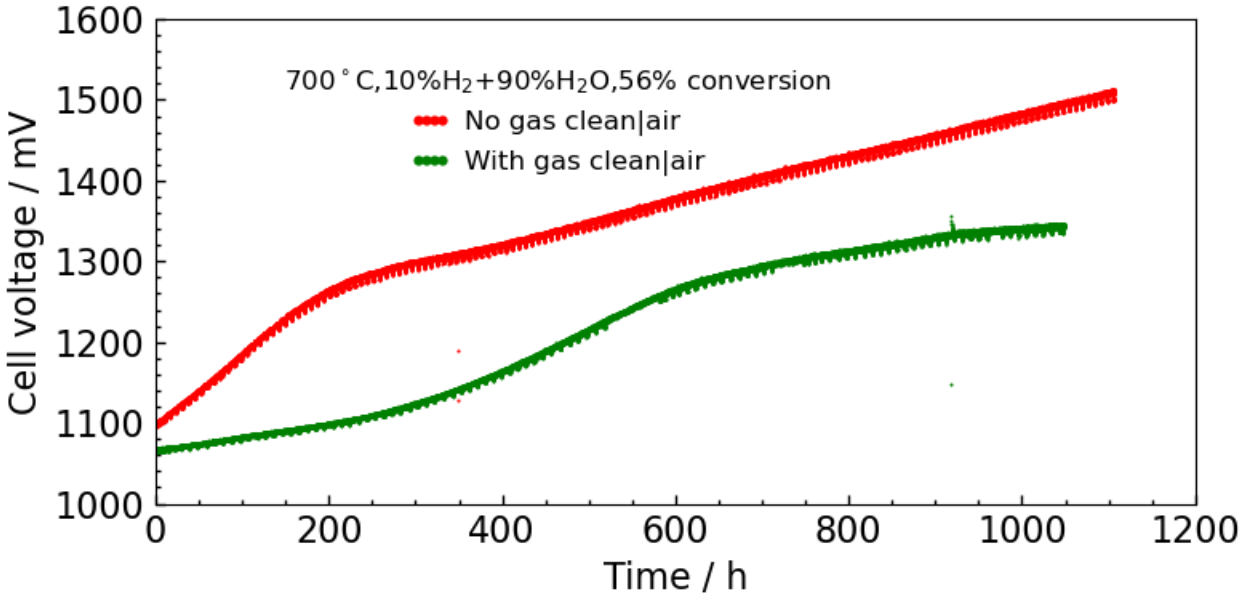


Figure 5: Cell voltages development as function of testing time for the cells tested with and without gas cleaning

Table 4: Calculated overall and last 200 hours degradation rates of the tests with and without gas cleaning

Degradation mV/kh	No cleaning	With cleaning
Overall	370	264
Last 200h	260	109

The serial resistance Rs, polarization resistance, Rp and area specific resistance, ASR extracted from the impedance data are plotted in Figure 6. It can be seen that cell without gas cleaning showed a fast initial Rp degradation, however at the end of the tests, both cells reached almost the same Rp values, and the main difference in the degradation is due to the Rs, where cell without gas clean showed a higher Rs degradation rate than the one with gas cleaning. The overall degradation rates of both cells are summarized in Table 5.

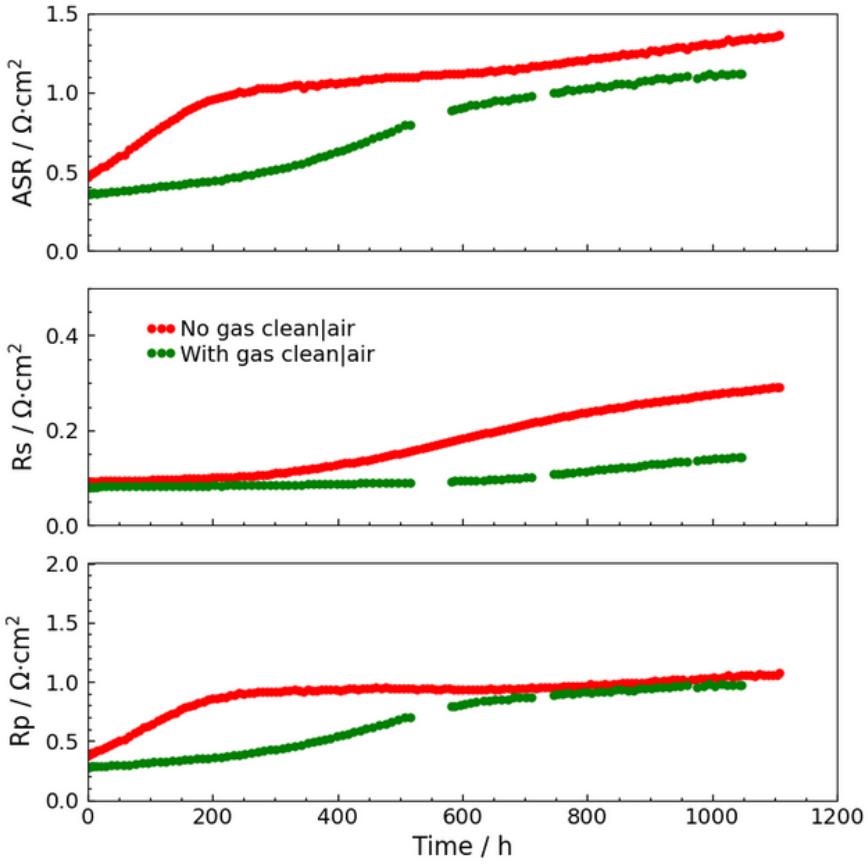


Figure 6 : Serial resistance Rs, polarization resistance and area specific resistance extracted from the impedance spectra measured during the durability operation for the two tested cells.

Table 5: Rs, Rp and ASR extracted from the impedance spectra measured during the durability operation of the two tested cells with and without gas cleaning.

Resistance Degradation Ω.cm²/kh	Clean	No clean
Rs	0.06	0.18
Rp	0.66	0.63
ASR	0.72	0.81

The impedance spectra and DRT analysis of the impedance measured during the durability operation are presented in Figure 7. Both cells have increased ASR after durability operation, however compared with the test with gas cleanning, the one without gas cleanning exhibits larger ASR increase, as well as a larger DRT peak increase at the high frequency range (10-100KHz). The results indicate that cleaning the gas can reduce the SOEC degradation.

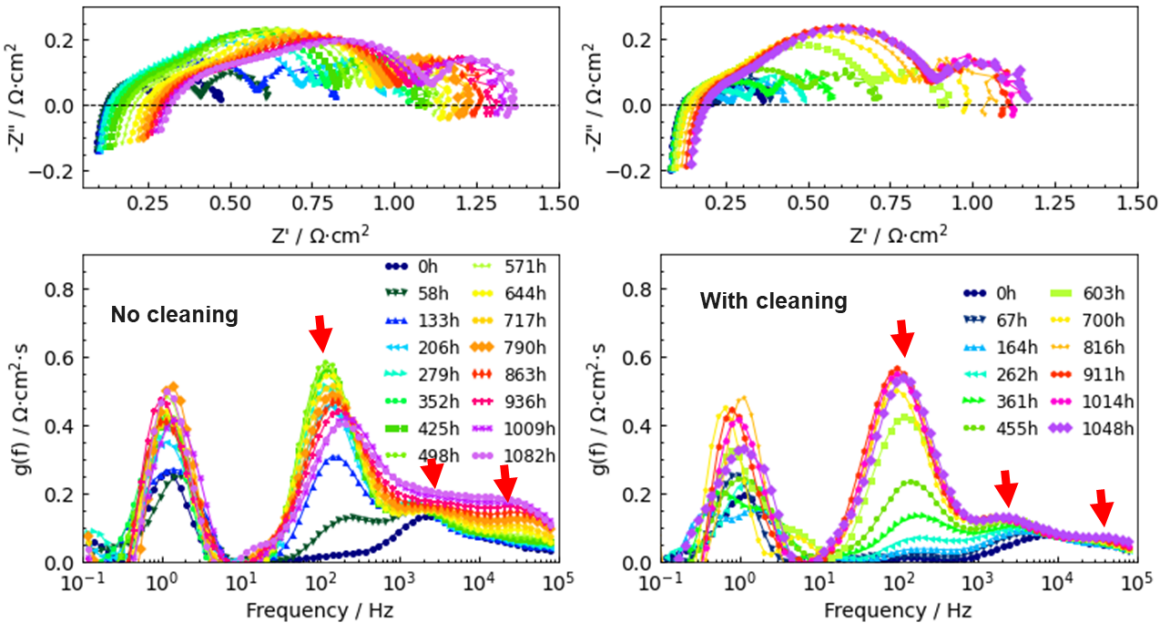


Figure 7 : EIS and DRT of the impedance measured during the durability tests

4.3 Effect of current density

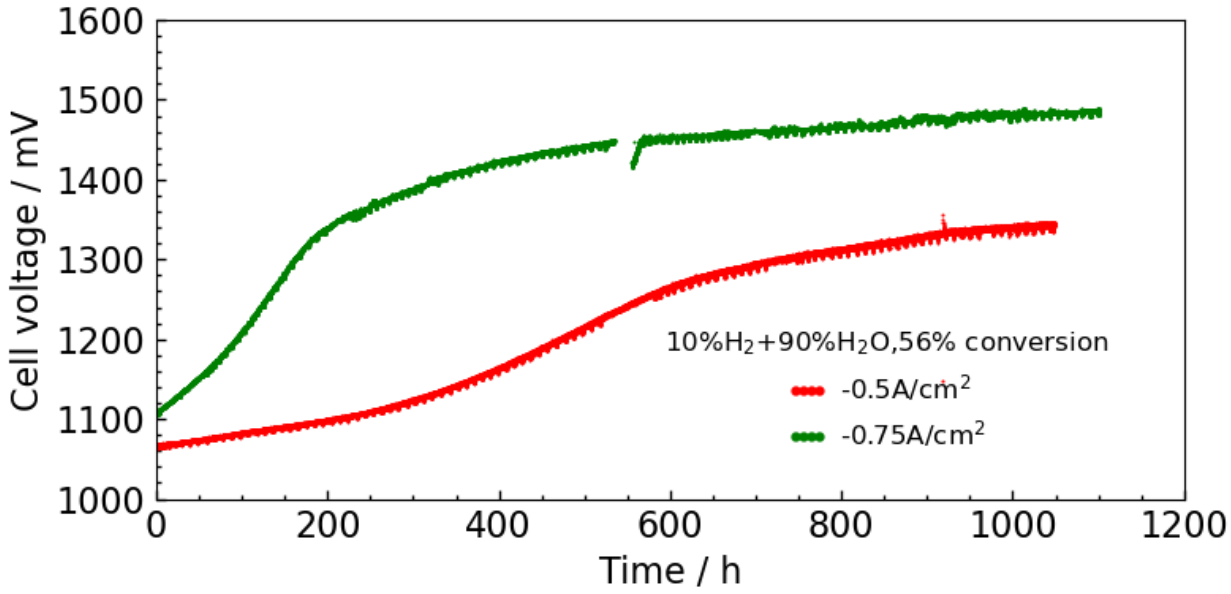


Figure 8: Cell voltage evolution as function of time under different current densities

To study the effect of the current density on the cell degradation, two cells were tested under -0.5 and -0.75 A/cm² respectively. The voltage degradation rates of both tests are summarized in Table 6. Operating the cell under higher electrolysis current density resulted in a higher overall degradation rate, but a lower degradation rate in the last 200 hours, indicated that high current density may accelerate cell initial degradation, potentially reach a steady state degradation in a shorter time.

Table 6: Overall and last 200h degradation rates of the two tests at -0.5 and -0.75 A/cm2.

Degradation mV/kh	-0.5 A/cm²	0.75 A/cm²
Overall	264	341
Last 200h	109	44

Figure 9 presents the EIS and DRT analysis and comparison of both tests. It can be seen from the EIS that the cell operating at -0.75A/cm² showed a larger ohmic resistance increase compared with the cell operating at -0.5A/cm². Large low frequency loops with positive imaginary value can be clearly seen after 250 hours operation at -0.75A/cm², however such loop only appeared on the cell operated at -0.5A/cm² after 700 hours operation and with rather small size, such a loop may be related to the reduction of ZrO_2 in the fuel electrode. From the DRT plots it can be seen that both cells have similar degradation process, i.e. the high frequency process at frequency (>10 kHz) and middle frequency at 1K -10 kHz and 10-1 kHz) and such processes may be attributed to the fuel electrode degradation. Operating the cell at lower current density exhibits lower overall degradation rates.

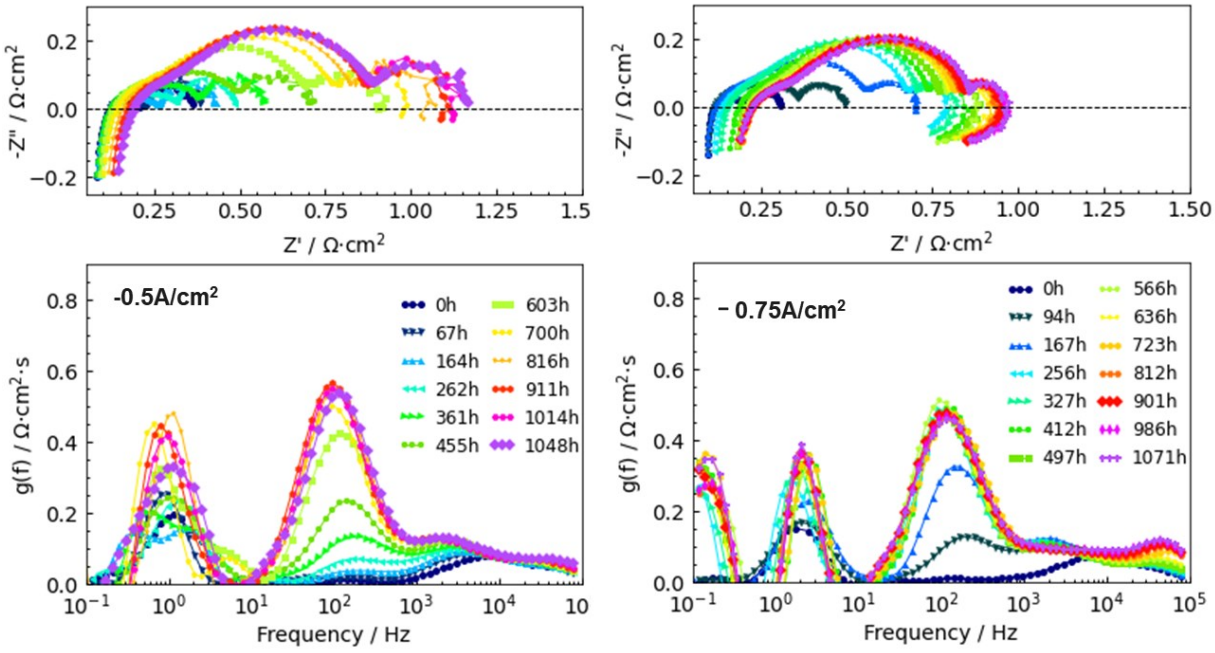


Figure 9 : EIS and DRT analysis of the impedance measured during the durability test

4.4 Effect of steam utilization

Three cells have been tested to study the effect of steam utilization on the cells' degradation. The tests were performed at 700 °C with 10% H2 + 90% H2O supplied to the fuel electrode and air supplied to the oxygen electrode under current density of -0.5A/cm2, fuel electrode gas flow was adjusted in order to reach the H2O

conversion of 56%, 40% and 28%. The cell voltages evolution as a function of testing time are presented in Figure 10. The test for 28% steam utilization is still ongoing. The overall degradation rates and degradation rates in the last 200h tests are calculated based on the voltages measured during the durability test and presented in Table 7. It can be seen that reducing the steam utilization, the overall degradation decreases. For the 40% steam utilization test, the cell reached to steady state with almost no degradation in the 400 hours. For the cell tested at 28% utilization, the cell exhibits a linear degradation in the last 400 hours, nevertheless the overall degradation is still lower than the high utilization tests.

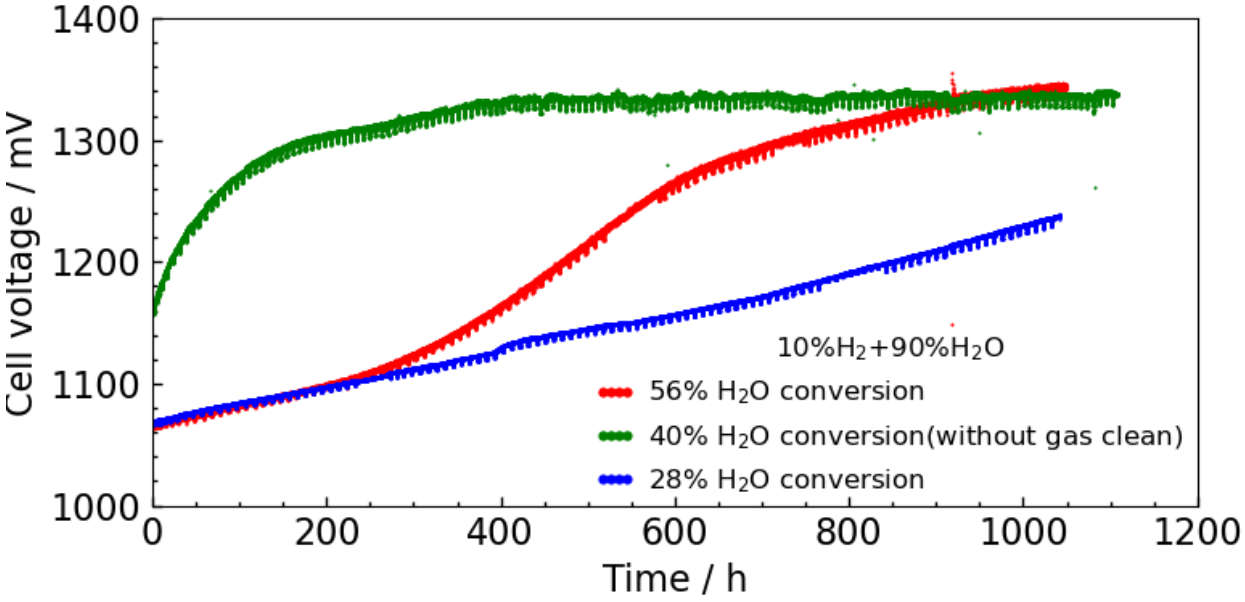


Figure 10: Cell voltages evolution as function of testing time for the three cells tested at 56%, 40% and 28% of steam utilization

Table 7: Overall and last 200h degradation rates of the three tests at 56%, 40% and 28% steam utilization

Calculated degradation rates	Steam utilization/conversion		
	56%	40%	28%
Overall, mV/kh	264	160	147
Last 200h, mV/kh	109	-2	197

The Rs, Rp and ASR extracted from the EIS measured during the durability test are presented in Figure 11. It can be seen that the 40% H_2O utilization test has higher Rp since the beginning of the durability test, which was due to the degradation during the fingerprint. However, the Rs of the three tests are similar where the 56% H_2O test case has slightly lower Rs but higher Rp than the 28% utilization test, and the two tests resulted in a similar ASR and similar initial cell voltage as shown in Figure 12. Table 8 presents the calculated Rs, Rp and ASR degradation rates. It can be seen that the lower the utilization, the less the ASR degradation rate and with low Rs degradation rates means that less microstructural degradation (e.g. Ni migration from the active area to the supporting layer).

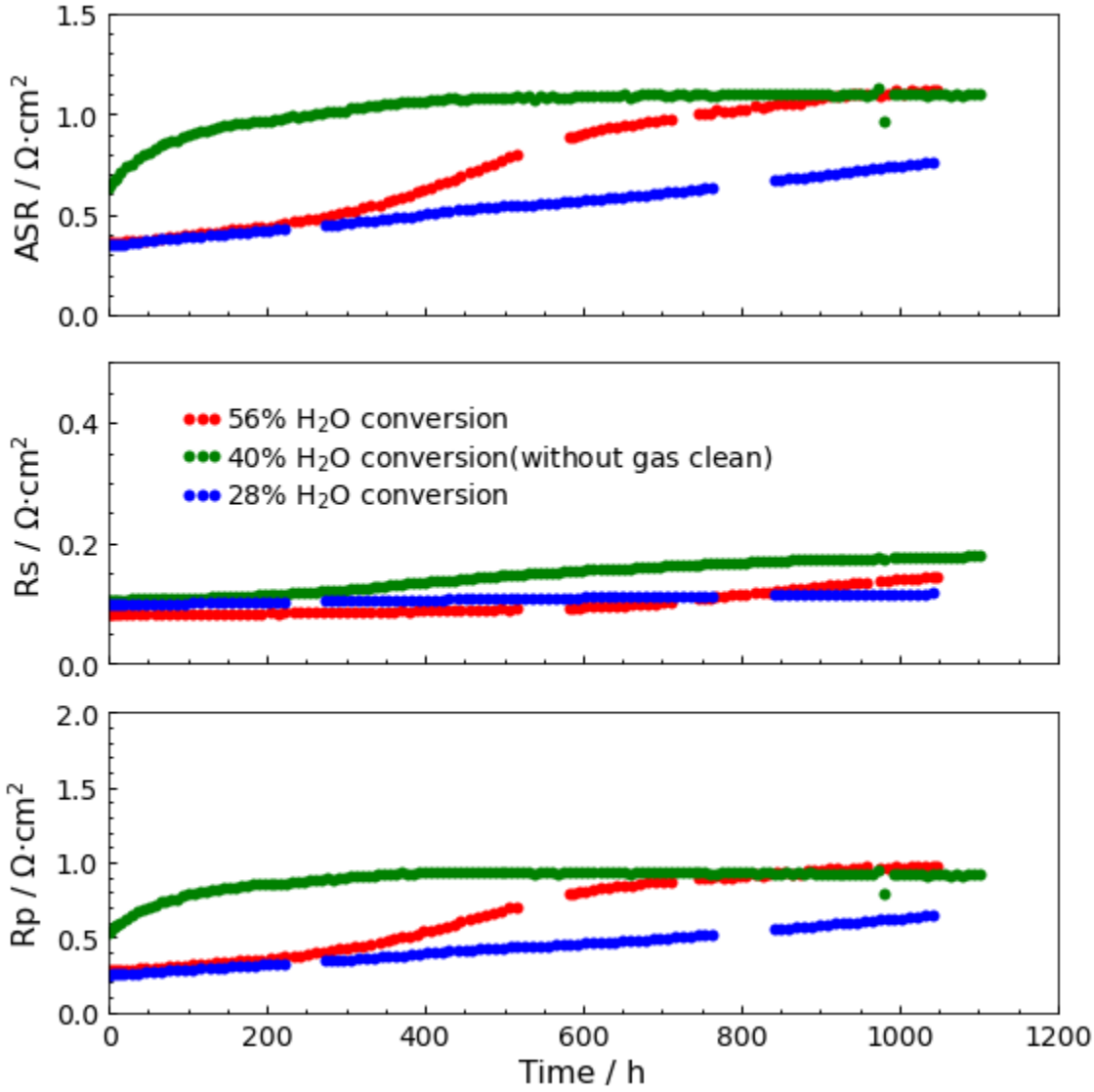


Figure 11: Serial resistance, polarization resistance and ASR extracted from the EIS measured during the durability test.

Table 8: Rs, Rp and ASR degradation of the cells tested at 56%, 40% and 28% reactant utilization

Resistance Degradation Ω.cm²/kh	56%	40%	28%
Rs	0.06	0.07	0.02
Rp	0.66	0.35	0.38
ASR	0.72	0.42	0.4

4.5 Effect of gas composition

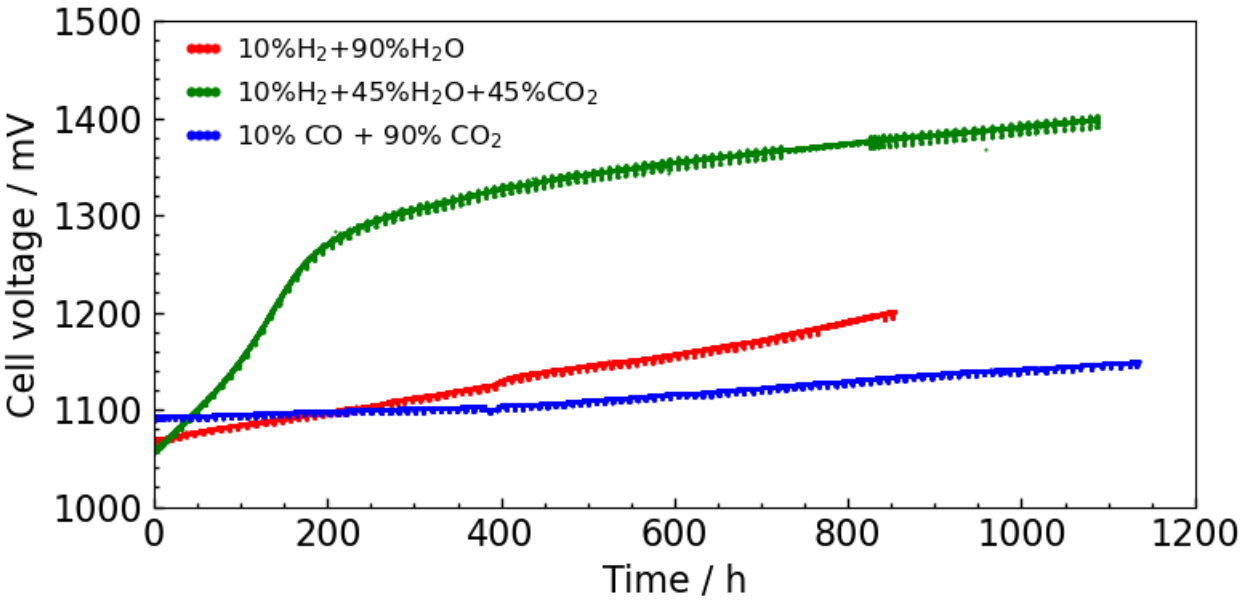


Figure 12: Cell voltages evolution as function of testing time for the three cells tested at for steam electrolysis, c o-electrolysis and CO2 electrolysis.

The effect of fuel electrode inlet gas composition on the cell durability was studied at 700 °C, -0.5A/cm^2 and 28% of reactant utilization. Three inlet gas composition was, 10%H_2 + 90%H_2O for steam electrolysis, 10% H_2 + 45% H_2O +45% CO_2 for co-electrolysis and 10% CO + 90% CO_2 for CO_2 electrolysis. The low reactant utilization was chosen to avoid the potential carbon formation. The starting voltages are similar for steam electrolysis and co-electrolysis, but slightly higher for CO_2 electrolysis which is as expected since more energy is required for splitting CO_2 than H_2O. On the other hand, CO_2 electrolysis showed a linear degradation rate with the lowest overall degradation; co-electrolysis exhibits a fast initial degradation rate in the first 200 hours and a linear degradation afterwards. The degradation rates of steam electrolysis lie in between co-electrolysis and CO_2 electrolysis. The overall degradation rates and degradation rates in the last 200 hours are summarized in Table 9 .

Table 9: Rs, Rp and ASR degradation of the cells tested for steam electrolysis, co-electrolysis and CO2 electrolysis.

Calculated degradation rates	Electrolysis mode		
	H_2O electrolysis	Co-electrolysis	Co2-electrolysis
Overall, mV/kh	156	310	52
Last 200h, mV/kh	178	64	48

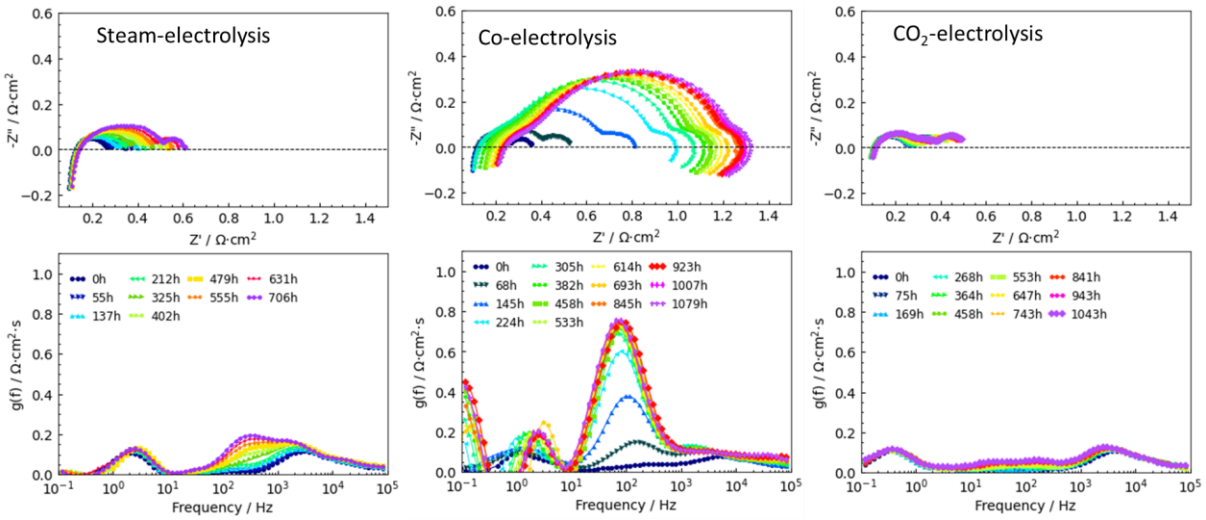


Figure 13: EIS and DRT analysis of the impedance measured during the durability test for steam electrolysis, co-electrolysis and CO2 electrolysis.

Figure 13 presents EIS and DRT analysis of the impedance spectra measured during the durability test. From the EIS figures only minor Rs change can be seen for the steam electrolysis and CO_2 electrolysis, but large Rs increase is seen for the co-electrolysis test. On the other hand, small polarization increase is seen for the CO_2 electrolysis but large polarization increases are seen on both steam electrolysis and co-electrolysis. The DRT analysis shows peak increase at frequency range of 10-1kHz on all the three cells, with an order of co-electrolysis superior to steam electrolysis superior to CO_2 electrolysis. The results indicated that co-electrolysis resulted in highest degradation rates while CO_2 electrolysis showed the lowest degradation rates.

5 Post-test analysis

Post-test analysis were performed on some of the tested cells. Figure 14 shows the cross-section of polished sample microstructure of the cell used in this project. The cell has a thick fuel electrode support layer with large porous and high porosity and a thin fuel electrode with low porosity and fine microstructure, a thin dense electrolyte and a thin oxygen electrode.

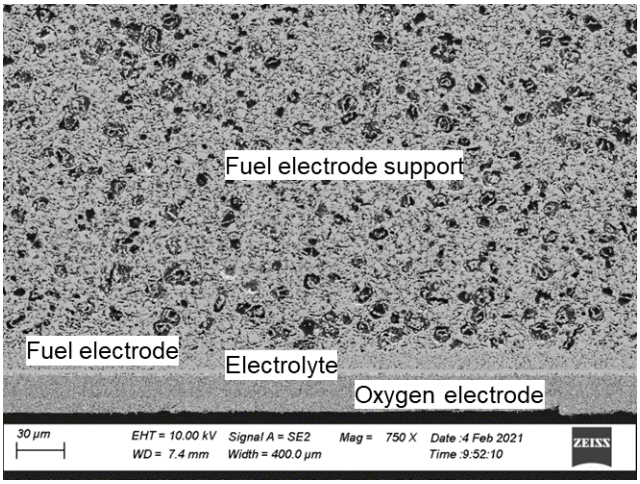


Figure 14 : Microstructure of the cells tested in this project

Scanning Electron Microscopy (SEM) analysis were carried out on 4 of the selected tested cells. The tested cells were fractured, and the fracture surface were polished and coated with carbon coatings. Figure 15 presents the SEM of the 4 samples. The reference cell only experienced the initial fingerprint, the other three cells were operated at 700 °C -0.5A/cm^2, with 10% H_2 + 90% H_2O supplied to the fuel electrode compartment. The voltage degradation during the operation for the three durability tested cells can be found in Figure 5 red line for without gas cleaning 56% conversion, green line for with gas cleaning 56% conversion and Figure 10 green line for 40% conversion without gas cleaning. It can be seen that the major difference between the tested cells and reference cell is the presence of more black dots (marked in the red circle) in the Ni grain. No noticeable difference is seen between the tests with and without gas cleaning. Nevertheless, the results indicate that the enrichment of Si is related to the long-term electrolysis process.

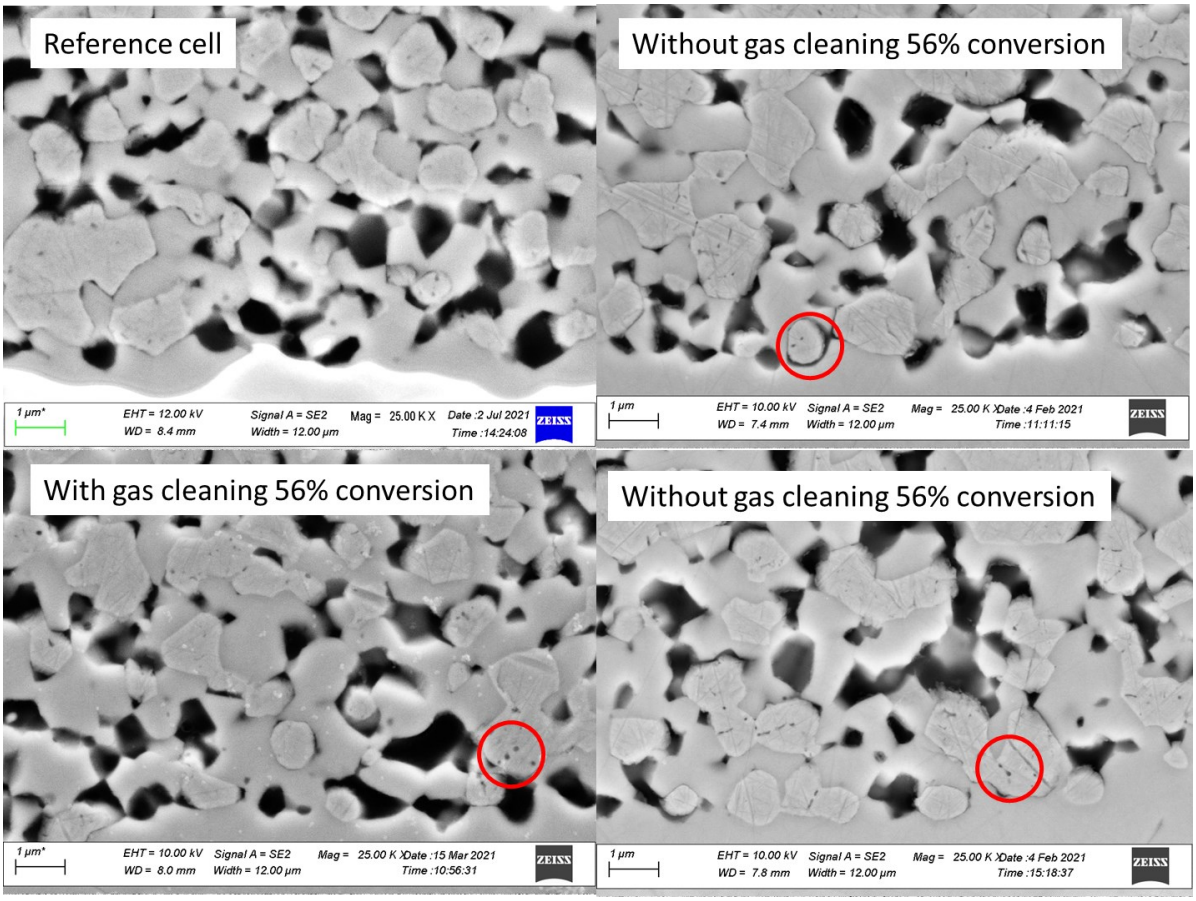
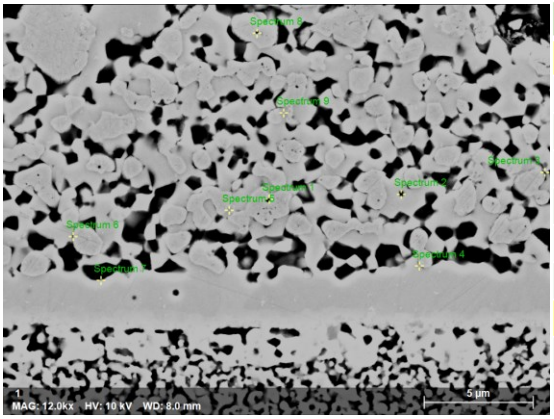


Figure 15: SEM analysis of the four selected cells. Red circle indicate the black dots in the Ni grains

Energy dispersive X-ray spectroscopy (EDS) point analysis were performed on the fuel electrode of the cell tested with gas cleaning, and the element ratio of the analysis is summarized in the right table of Figure 16. It can be seen that the black dots, in EDS analysis point 1 and 8 mainly contain SiO_2.



Point / at.%	Ni	Zr	Y	O	Si	Al
1	92.11	1.16	-	3.93	2.78	0.02
2	14.18	60.38	7.1	17.75	0.48	0.11
3	6.34	60.72	8.13	24.36	0.36	0.08
4	67.64	21.62	2.75	7.72	0.16	0.1
5	32.87	43.68	5.3	17.98	0.17	-
6	76.48	15.82	1.95	4.99	0.62	0.14
7	0.38	66.73	8.89	23.6	0.28	0.12
8	91.3	0.89	-	4.44	3.37	-
9	40.49	38.34	4.45	16.51	0.13	0.07
10	0.3	72.29	8.24	19.73	0.33	0.1

Figure 16: EDS point analysis of the fuel electrode of the cell tested with gas cleaning

In order to find the source of Si, [**ELCOGEN**] has performed the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis on the raw materials as well as the as-prepared cells and the results are shown in Table 10. The results show that the Si concentration is below the measurement limitation (10 mg/kg) in the cell raw materials. It is therefore hardly to conclude the Si source.

Table 10: ICP-MS analysis results of the Si concentration in cell materials

Sample name	Unit	Result
HM NiO	mg/kg *	<10
SMM NiO	mg/kg *	<10
NiO/YSZ	mg/kg *	<10
ACT-2 in, batch 4309-3	mg/kg *	<10
INK-CON-1, batch 4275-2	mg/kg *	<10
ELC-4 ink, batch 4301-3	mg/kg *	<10
8YSZ	mg/kg *	<10

* External ISO/IEC 17025 accredited service provider
# Accredited method

6 Conclusion

In this report, we summarized the effect of different operation condition on the SOECs degradation. The results show that [**ELCOGEN**]cell gave excellent initial performance and the specific fuel production energy consumption calculated from the initial iV characterization at 700C, -0.5 A/cm^2 is 2.3, 2.32 and 2.41 kWh/m^3 for H_2 production, H_2 + CO production and CO production, which is below the project final targeted value of 2.9 kWh/m^3. Degradation rate can be reduced by increasing temperature and by decreasing reactant utilization and current density. Cleaning of inlet gas can reduce the initial degradation. Studies on the purges on the oxygen electrode show no remarkable difference of degradation between using Air or no gas to the oxygen electrode, but CO_2 purge gas resulted in a oxygen electrode degradation, even though the degradation could be partially regenerated by stopping the CO_2 purge. Regarding the inlet gas composition, the results show that CO_2 electrolysis has the lowest overall degradation, but co-electrolysis shows higher degradation rates than CO_2 electrolysis. Impedance analysis shows that the degradation is mainly associated to the fuel electrode process at ca. 100-1kHz frequency range.

SEM analysis on the long term tested cells found more SiO_2 enrichment in the Ni grains than the reference cell which only experienced initial performance characterization. However, ICP-MS analysis show that the SiO_2 concentration is below 10 ppm for the raw materials and the as-prepared cells. Since the Si enrichment does not differ too much between the test with and without gas cleaning, it is therefore hard to conclude the source of Si, more analysis is undergoing to check the Si origination.

Based on the unit cell tests, it is therefore recommended to operate the SOEC stack and demonstration system to high temperature and low steam utilization as well clean the inlet gas in order to improve the stack lifetime.