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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

D2.6 – 5000 hours durability test of SOEC under relevant operation conditions

WP2 – High temperature electrolysis development

Project information

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Deliverable report

1 Executive Summary

1.1 Description of the deliverable content and purpose

This deliverable presents the results of the 5000 hours long term operation of SOEC.

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

Long term operation of SOEC is required to study the degradation mechanism of the SOECs. Most of SoA durability studies were performed around 1000 hours, which is too short to reveal the long-term behavior of the SOECs. This study shows that even though the cell has a high initial degradation rate, but in the long-term operation, the cell exhibited nearly zero degradation over the last 4000 hours.

1.3 Corrective action (if relevant)

N/A

1.4 IPR issues (if relevant)

N/A

2 Introduction

Commercial SOEC generally requires a stable operation for at least five years. Many of the SoA SOEC test results presented today are limited to around 1000 hours. Testing of SOEC for a longer period is desired to be able to reveal the long-term degradation behavior, since it may take a few hundred hours for the cell to pass through the initial degradation stage. Long-term SOEC operation on [**ELGOGEN**] cell has not been reported so far. In this work, we demonstrate the durability of [**ELCOGEN**] cell for electrolysis operation of more than 5000 hours under constant operation condition at ambient pressure.

3 Experiment

In this work, an [**ELCOGEN**] solid oxide cell was tested with the high-pressure test station developed at [**DTU**]. The cells consists of a ~400 µm Ni/YSZ (yttria stabilized zirconia) support layer having a ~12 µm Ni/YSZ active layer, a ~3µm YSZ electrolyte and a CGO (gadolinium-doped ceria) barrier layer of similar thickness and a ~12 µm thick LSC (lanthanum strontium cobaltite) oxygen electrode[2]. For testing, the cell was mounted in an alumina cell test house[3]. Ni plates and Ni meshes were used as fuel electrode current collector and gas distribution component; Au plates and Au meshes were used as oxygen electrode current collector and gas distribution components. An Au frame was used for sealing the fuel electrode compartment and no sealing was applied for the oxygen electrode side. The cell test house was then placed in the furnace which is located inside the high-pressure vessel. The cells were heated to 850 °C with a ramp rate of 1 °C/min, 20 L/h N_2 were supplied to the fuel electrode compartment and 20 L/h air were supplied to the oxygen electrode during heating. The NiO in the cell was reduced in 20 L/h of 5% H_2 + N_2 for 2 hours then H_2 + 4% H_2O for 1 hour. The cell temperature was then brought to 800 °C for initial performance characterization. The initial performance characterization was done from 800 to 650 °C with 50 °C /step in 24 L/h H_2 with 4, 20, 50, 90% H_2O supplied to the fuel electrode and a 100 L/h of air flow supplied to the oxygen electrode. Current-voltage curves (iV) and electrochemical impedance spectra (EIS) characterization were carried out at each characterization point. EIS were measured at zero current (open circuit voltage) using a Solartron 1255B frequency analyzer and an external shunt connected in series with the cell. The spectra were recorded from 96850 to 0.08 Hz with 12 points per decade and were corrected using the short circuit impedance response of the test setup. From the impedance spectra, the ohmic (serial) area specific resistance (R_s) was taken as the value of the real part of the impedance measured at 96850 Hz and the polarization area specific resistance (R_p) was taken as the difference in the real part of the impedance at 96850 Hz and 0.08 Hz. The total area specific resistance of a cell was calculated as the sum of the real part of the impedance ($R_s + R_p$).

After initial performance characterization, the cell temperature was changed to 700 °C for durability study. The durability test was carried out at ambient pressure, -0.5A/cm^2 with 50%H_2 + 50% H_2O supplied to the fuel electrode and 100L/h Air supplied to the oxygen electrode. The test conditions were selected based on the previous tests results in **deliverable D2.2** report, where Si impurities and migration of Ni was seen in the tested samples, and it was speculated that increasing the H_2 content in the fuel stream could reduce the Ni and Si mobility, thus potentially lead to a longer lifetime. Impedance spectra were recorded during the durability test.

4 Results

4.1 Cell voltage

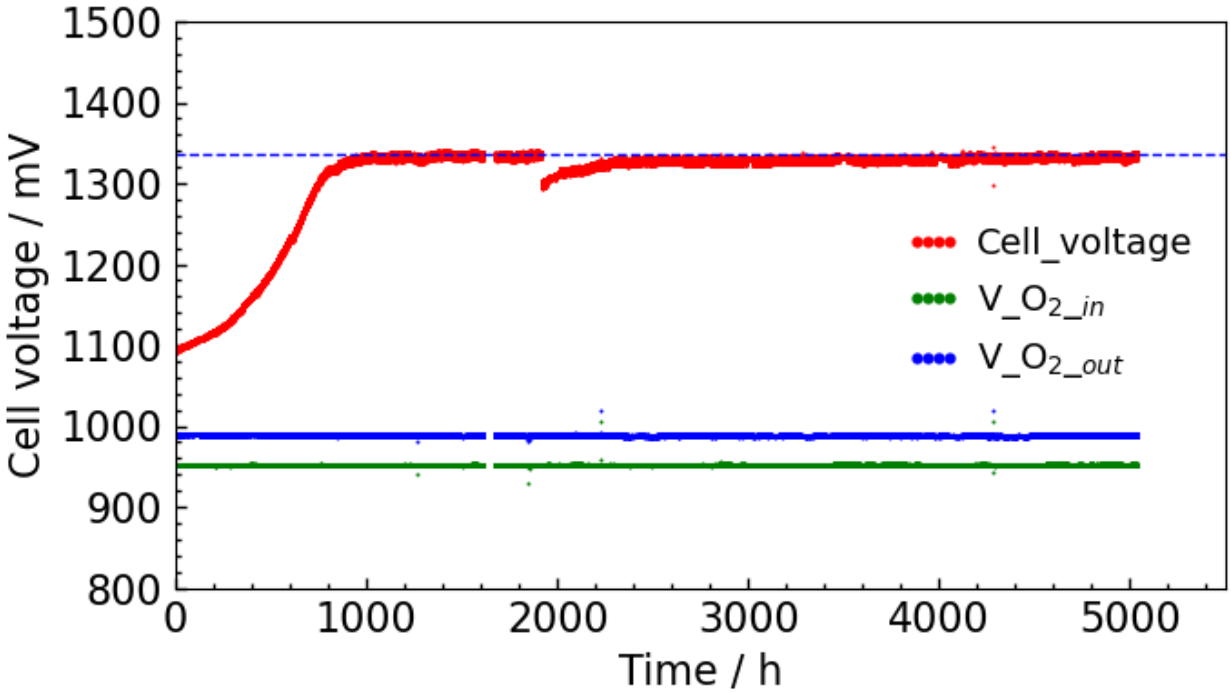

Figure 1:Cell voltage, inlet and outlet oxygen sensor voltage evolution as function of testing time. The cell was tested at 700 °C, -0.5A/cm² with 50%H₂ + 50%H₂O supplied to fuel electrode compartment and Air supplied to the oxygen electrode compartment.

Figure 1 presents the cell voltage evolution during the entire durability operation. The durability test was performed at ambient pressure, 700 °C, -0.5A/cm^2 with 50%H_2 + 50%H_2O supplied to fuel electrode compartment and Air supplied to the oxygen electrode compartment. For checking the leak of the cell, oxygen partial pressure was measured via two zirconia oxygen sensors that placed at the inlet and outlet of the fuel gas streams respectively. The measured voltages are also plotted in Figure 1. It is clear that during the operation, overall no changes were observed on the voltage of the oxygen sensors at the inlet and outlet of the fuel stream, indicated the gas tightness of the sealing and the cell. The test experienced a short interrupt at ca. 1900 hours with a few minutes' gas and current cutting off, the test was resumed after resetting. Overall, the cell showed a fast initial degradation in the first 900 hours, with a voltage increase from ca. 1090mV to 1330 mV and a degradation rate of 263mV(24%)/1000 hour. The cell voltage was afterward stabilized around 1330 for the rest of the test with nearly 0 degradation rate, for better viewing, a blue dot line at cell voltage of 1335mV was plotted in Figure 1.

4.2 Electrochemical impedance spectra

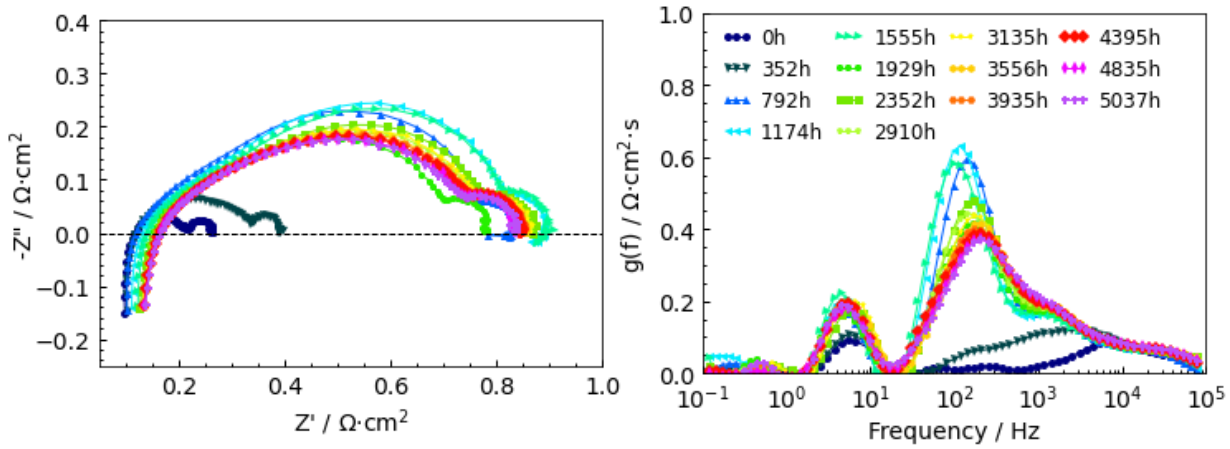

Figure 2: Electrochemical impedance spectra (EIS) and DRT analysis of the EIS measured during the durability test

Electrochemical impedance has been recorded during the durability operation. Analysis of Distribution of relaxation time (DRT) method was employed to help identify the degradation processes. The Nyquist and the DRT plots are presented in Figure 2. From the Nyquist plot, the Rs has a relative small change but a huge change on the polarization resistance with almost 4 times increase can be seen. Such a large change takes place in the first 1200 hours. DRT reveals three major peak changes. Two peaks at 100 Hz-1 kHz and 1 k - 10 kHz can be mainly attributed to the fuel electrode process and one peak at 1-10Hz can be attributed to gas conversion process. The first 1200 hours fast degradation mainly contributed from the fuel electrode. A long-term activation/stabilization can be observed on both of the fuel electrode and gas conversion processes after the initial degradation. The activation process might be related to the change of impurities covering the fuel electrode, such as crystallization of Si impurities that could lead to activate sites recovery.

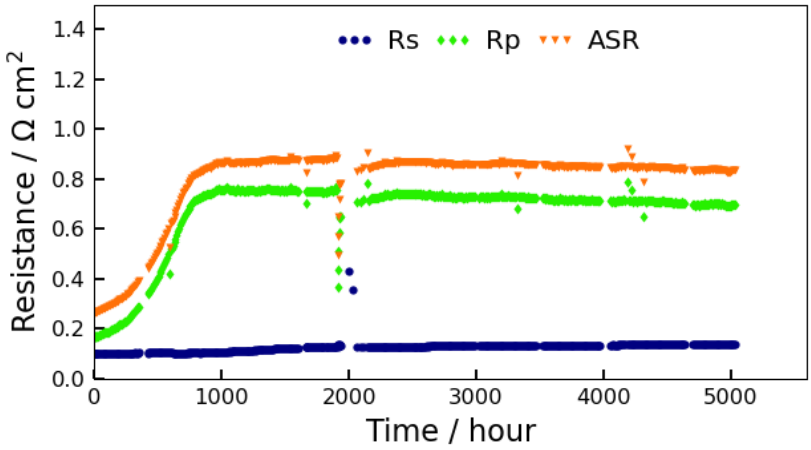

Figure 3: Rs, Rp and ASR extracted from the impedance measured during the durability test

Figure 3 presents the Rs, Rp and ASR extracted from the impedance measured during the durability test. It can be seen that Rs has a quite low degradation in the entire operation period with an overall degradation rate of 8mΩ cm²/1000h. On the contrary, Rp showed a very fast initial degradation in the first 900 hours with a

degradation rate of 642 mΩ cm²/1000h, which may be related to Ni coursing/migrating together with Si impurity poisoning. After the fast initial degradation, a slight activation of Rp was observed from 1000 hours to the end of the test, with an overall degradation rate of -16 mΩ cm²/1000h.

5 Microstructure analysis

SEM analyses were performed on the cell from inlet to outlet and are presented in Figure 4 and zoomed in Figure 5. No crack or detachment was seen in the cell. However, a change of porosity through the cell can be seen in Figure 4. Especially in the fuel electrode as highlighted in the red square in Figure 5. Where inlet has slightly higher porosity than middle and outlet of the cell. Loss of Ni in the area close to electrolyte (under the red square) can be seen especially at the inlet of the cell, which explains the degradation of the fuel electrode as seen in the DRT plot in Figure 2. No visible change in the oxygen electrode was observed (see top part in Figure 5).

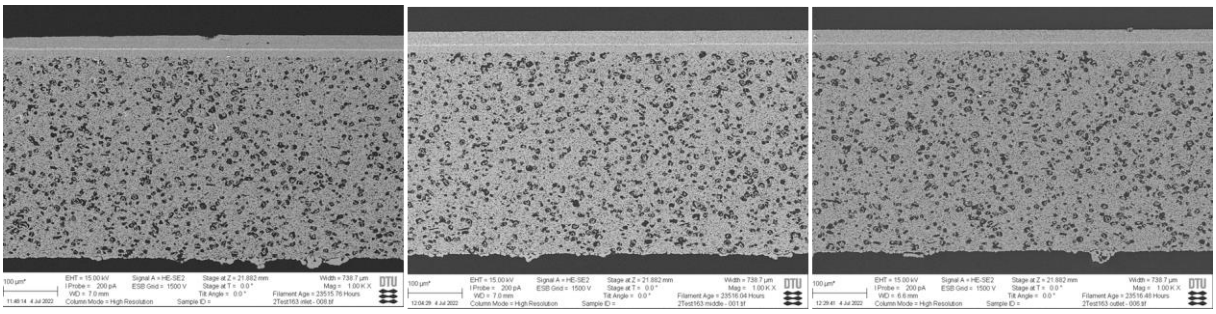

Figure 4: SEM analysis of the cells after testing, from left to right: fuel electrode gas inlet, middle and outlet of the cell.

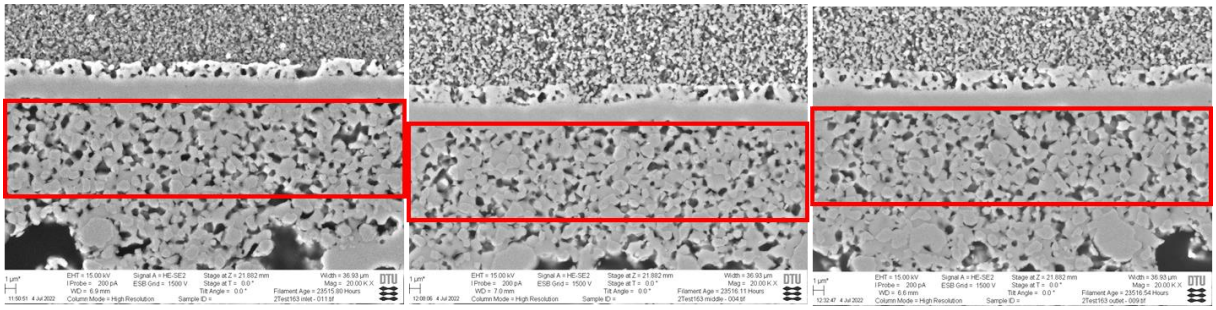

Figure 5: SEM analsyis zoom-in of the cell after testing, from left to right: fuel electrode gas inlet, middle and outlet of the cell.

In the Ni grains, few black dots are visible; they were identified as Si inclusions in **deliverable D2.2**. In the testing conditions of the present deliverable, the overall concentration of these Si inclusions seems lower compared to what was observed on the fuel electrode tested with high steam concentration, in D2.2.

6 Conclusion

This work presents the results of 5000 hours durability test of an [**ELCOGEN**] cell. A fast initial degradation in the first 900 hours operation was observed, and almost no cell voltage degradation in the last 4000 hours operation. Impedance analysis results show that the main degradation was due to the middle frequency process at a frequency range of 100-1kHz mainly related to fuel electrode degradation. Nevertheless, the nearly 0 voltage degradation in the last 4000 hours operation indicates that [**ELCOGEN**] cell presents an excellent stability under such operating conditions. Post-test SEM images review the decrease of porosity from the fuel gas inlet to the fuel gas outlet of the cell, indicating the degradation of the fuel electrode. Less amount of visible Si in the Ni grain was observed compared to the tests performed with high steam concentration inlet as reported in **deliverable D2.2** report, which indicates that increasing the H_2 concentration and lowering the steam partial pressure can delay the Si and Ni mobility, and thus can enable a long cell lifetime.