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

Deliverable

D2.5 – Influence of pressure on the 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

This deliverable deals with the effect of operation pressure on the SOEC's performance and durability.

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

State-of-the-art SOEC operation are mostly performed under ambient pressure. Operating SOEC at elevated pressure has the advantage that pressured H₂ can be produced on the cell, thus less energy is required for the downstream process.

1.3 Corrective action (if relevant)

Non applicable

1.4 IPR issues (if relevant)

Non applicable



2 Introduction

Operating of SOEC at high pressure possesses several advantages 1) improving the SOEC performance by reducing the area specific resistance (ASR) 2) pressurized downstream fuel gas produced directly, and less energy required for pressurization by evaporating liquid water as compared to pressurizing the produced gas 3) better heat integration with the downstream processing unit such as catalytic reactor for synthetic fuel production. The global efficiency of high pressure SOEC is expected to be 3-4% higher than the ambient SOEC system[1]. However the development of high pressure SOEC is still in the early stage as most of the R&D are focusing on the ambient pressure operation. The overall objective of this deliverable is to demonstrate the effect of pressure on SOEC's performance and durability. Pressure during tests (up to 15 bar) was chosen according to the objective related to the SOEC system.

3 Experiment

In this work, an [ELCOGEN] solid oxide cell was tested with the high-pressure test station developed in [DTU]. The cell 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 as shown in Figure 1. The cells were heated to 850 °C with a ramp rate of 1 °C/min. 20 L/h N2 was supplied to the fuel electrode compartment and 20 L/h air was supplied to the oxygen electrode during heating. The NiO in the cell was reduced in 20 L/h of 5% H₂ + N₂ for 2 hours then H₂ + 4% H₂O for 1 hour. The cell temperature was then brought to 800 °C for initial performance characterization. The initial performance characterization was performed from 800 to 700 °C with 50 °C /step in 24 L/h H₂ with 4, 20, 50, 90% H₂O 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 kept at 700 °C, iV and EIS were carried out under different pressures. Pressurized N₂ was used as compression gas and the detailed operation of the high pressure setup can be found in [4]. Durability tests were started by operating the cell firstly at 50%H₂ + 50% H₂O then 20%H₂ + 80% H₂O and finally 10%H₂ + 90% H₂O. The reduction of the H₂ concentration in the fuel gas



composition was aimed at avoiding a high H₂ leak at high flow/concentration that was observed during the operation. This is explained in more details in section 3.2.1.



Figure 1: High pressure single cell test setup at [**DTU**] Energy



3.1 Initial performance characterization

Figure 2: Nyquist electrochemical impedance spectra measured at different pressures (left) and DRT analysis of the impedance (right). The EIS were recorded at 0A/cm², 700°C with 50%H₂ + 50% H₂O supplied to the fuel electrode and Air supplied to the oxygen electrode.

Electrochemical impedance spectra (EIS) and current-voltage (iV) curves were recorded at each pressure to study the pressure effect on the cell's performance. Figure 2 (left) presents the Nyquist plot of the impedance spectra and Figure 2 (right) presents the corresponding distribution of relaxation time analysis (DRT) results of the impedance. The impedance was measured at 700°C with 50%H₂ + 50% H₂O supplied to the fuel electrode and air

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supplied to the oxygen electrode compartment. It can be seen on the Nyquist plot that pressure has no effect on the Ohmic resistance (Rs) of the cell, but has a beneficial effect on the polarization resistance (Rp), since the Rp decreases with the increase of the pressure. DRT analysis reveals two main peak process changes. The high frequency process with summit frequencies >1 kHz and a low frequency process with summit frequencies <1Hz. The high frequency process can be related to the fuel electrode process, where it is known that P_{H_2O} has a positive effect on the Ni electrode activity, as confirmed by the results. The lower frequencies correspond to the gas conversion process. The resistance is independent to the pressure in this area, but the gas conversion capacitance will be increased with pressure due to increased gas molecules surface coverage of the reactants on the electrode.



*Figure 3: iV characterization at different pressures. The iVs were recorded at 700°C with 50%H*₂ + 50% H₂O supplied to the *fuel electrode and Air supplied to the oxygen electrode.*

Figure 3 presents the effect of pressure on the iV characterization of the cell. The iVs show a nearly linear transition between solid oxide fuel cell (SOFC) mode (positive current) and SOEC mode (negative current). The OCV of the cell increases with the increase of pressure. Pressure has a clear positive effect on the SOFC mode where higher current density can be achieved at higher pressure, which agrees well with the impedance results shown in Figure 2. However in the electrolysis mode, pressure seems to have a negative effect in the maximum current output at current density < ca. $0.8A/cm^2$. The reason for this is that the pressure caused OCV increase, which has a larger effect on the cell voltage than the decrease of ASR (Cell voltage = OCV + current density × ASR).

3.2 Durability test results

3.2.1 Cell voltage

Durability test were carried out after the initial performance characterization. The voltage evolution during the durability test is presented in Figure 4. The tests were firstly started with 20%H₂ + 80% H₂O supplied to the fuel

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electrode compartment and current density at -0.5A/cm². However a large H₂ leak was discovered during high pressure tests. Because of this leak and as shown in Figure 5, the H₂ concentration inside the pressure vessel reached more than 20% of the lower explosive limit. In order to avoid further increase of H₂ concentration, the current was then reduced to 0.375A/cm². Further action was taken by changing the gas composition to 10%H₂ +90% H₂O for the rest of the test, which corresponds to a steam utilization of 42%. Moreover, from Figure 5 it is clear that the H₂ leak is current related but the source of the leak was not clear. It is however speculated that the high porosity of the fuel electrode may be the main source of leak, and such a leak can be prevented by applying a larger sealing area, i.e. by sealing both the edge of fuel electrode and the side of the electrode to avoid any H₂ outward diffusion through the porous fuel electrode. The test was interrupted after ca. 530 hours operation, due to the lab sensor service, which by accident caused a red alarm, with a consequence of a fast loss ca. 2 bar pressure in less than 1 minute. The test was continued without seeing a significant performance loss but a relative large voltage fluctuation/noise. It is speculated that the voltage noise was due to the small crack on the cell, which was caused by the sudden pressure drop. This can also be seen from the H₂ concentration in the pressure vessel, which showed in this period a relative lower and constant H₂ concentration. The test was stopped after 600 hours durability operation due to the failure of the N₂ compressor causing the 2 bar drop of pressure.



Figure 4: Cell voltage and pressure as a function of operation time

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Figure 5: Hydrogen concentration during the durability test

Even though there was an unexpected high H₂ leak during operation, the cell's performance was not influenced. The cell exhibited a high initial degradation rate at the first ca.300 hours of the test, and a very stable cell voltage of around 1315mV was observed with almost no degradation from ca.300 hours to the end of the test.

It is worth noting that the observed leak in this test does not imply that similar leak will be observed on the other cell or stack testing under either ambient pressure or high pressure, and is thus not expected to be an issue for the project final SOEC demonstration plant. The reason for such a leak observed in this high pressure test may be due to: 1) a very thin layer of glass sealing was used and only on the bottom edge of the fuel electrode in order to reduce Si poisoning from the glass, leading to less good gas tightness than in the stack; the leak from the cell edge can thus be prevented by applying a larger sealing area 2) the pressure vessel was pressurized by N₂, at high temperature the edge of the cell will be reduced by N₂ from NiO to Ni, which will produce micro-pores, thus increase the porosity of the cell edge; as a consequence a higher H₂ outward diffusion/leak rate will be seen compared with the cell operated with air as surrounding gas. And the leak from the cell cannot be burned due to the fact that there is no O_2 in the pressure vessel (it is N_2), therefore any amount of leak will be detected by the sensor placed at the outlet of the pressure vessel gas. The stack and the cell have different sealing method, therefore the detected leak from this cell test does not mean that the same extent will happen on the stack. Moreover, we did not observe any leak issues with [ELCOGEN] stacks testing in ambient pressure condition and they show very good gas tightness. Furthermore, the stack in the project final demonstration plant will be operated at ambient gas atmosphere. Thus, small amount of leak (if any) may be burned inside the furnace due to the high operation temperature.

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3.2.2 Electrochemical impedance spectra analysis



Figure 6: EIS and DRT of the EIS measured during the durability test at 15bara with 10% H₂ + 90% H₂O supplied to fuel electrode compartment and current density of -0.375A/cm².

Figure 6 presents the EIS and DRT analysis results of the impedance spectra measured during the durability test. For better comparison, only EIS measured with 10% H₂ + 90% H₂O supplied to fuel electrode compartment and current density of -0.375A/cm² were selected. It can be seen from low frequency arc of the EIS that even though the frequency ranges were the same as those measured in Figure 2a, but only half low frequency arc were measured from the impedance spectra. No ohmic resistance change was observed during the entire operation time, but fast polarization resistance increase can be seen in the first ca.300 hours operation. DRT analysis reveals that the polarization resistance increases mainly because of the high frequency process, where the frequency shifted from 2 kHz to ca. 100 Hz, and this process can be attributed to the fuel electrode process.



Figure 7: Rs, Rp and ASR evolution during the durability test

Figure 7 presents the Rs, Rp and ASR evolution during the durability test. During the entire durability operation period, very low degradation rate was observed on Rs with an overall degradation rate of $5m\Omega \cdot cm^2/1000h$. On



the other hand, the initial degradation of Rp seems independent to the gas composition or current density. A fast increasing of Rp was observed for the first 350 hours and followed by a reactivation process to the end of the test.

4 Post-test analysis

Cell microstructure overview



Figure 8: Cell microstructure overview from inlet to middle to outlet

Figure 8 presents the overview of the microstructure of the cell after test from inlet to middle to outlet. The pictures show that the cell remains intact after the high pressure tests; no cracks or delamination were observed in the electrolyte or electrode/electrolyte interface.

Fuel electrode SEM



Figure 9: SEM pictures of the fuel electrode (below the electrolyte) from inlet to middle to outlet

Figure 9 presents the SEM pictures of the fuel electrode, from the inlet to outlet. An increase of porosity was observed at the fuel electrode close to the electrolyte, indicating a Ni loss or Ni migration away from the fuel electrode towards the support layer. Similar degradation phenomena have been observed on similar cells from [ELCOGEN] tested at ambient pressure[5].

High resolution of the fuel electrode SEM is presented in Figure 10. It can be seen that Ni particles (with more scratch on the surface, e.g. the area marked with red in the inlet SEM) and YSZ particles (relative smooth surface) have a very clean interface, however small black dots (e.g. marked in the yellow line in the outlet SEM) were observed in the Ni grains, and have been identified to be SiO₂ impurity.

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Figure 10: high resolution SEM of fuel electrode

Figure 11 presents the SEM of the oxygen electrode from inlet to outlet, no appreciable microstructure change can be observed from inlet to outlet.



Figure 11: Microstructure of oxygen electrode from inlet to middle to outlet

5 Conclusion

In this work, the effect of pressure on the SOEC performance and durability was studied. The initial performance characterizations show that pressure has a positive effect on reducing the cell's ASR. However at electrolysis current density < 0.8A/cm², the performance improvement will be overtaken by the OCV increase due to the pressure. Long term operation of the cell at 700°C, 15 bara, -0.375A/cm² with 10%H₂ + 90% H₂O supplied to the fuel electrode compartment shows a fast initial cell voltage increase in the first ca. 300 hours operation, the cell voltage being stable afterwards. Impedance analysis reveals that the initial degradation was caused by the increase of cell polarization resistance, which is mainly due to the fuel electrode degradation. The overall degradation behavior is similar to the tests performed at 1bar.

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