D3.2; Report on individual components qualification tests

Public Summary

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Executive summary

This deliverable reports results on individual components as well as assembly's qualification tests performed in order to verify that each individual component and assembled parts (e.g. cells + seal, etc.) can maintain its integrity and functionality in pressurized electrolysis operation.
Non-destructive evaluation methods are selected based on protocols and criteria delivered in D3.1 to describe the work in GAMER and qualify manufacturing and integration of parts to form the single engineering unit (SEU) and finally, the hydrogen generator.
As the type of elements utilized for the construction of the primary components and assembled parts of the hydrogen generator is inherently dependent on the selected design of the SEU and final reactor, all materials taken into account were tested.

Contents

1 Introduction

1.1 The GAMER project

The GAMER project aims at developing a novel cost-effective tubular Proton Ceramic Electrolyser (PCE) stack technology integrated in a steam electrolyser system to produce pure dry pressurized hydrogen. The electrolyser system will be thermally coupled to renewable or waste heat sources in industrial plants to achieve higher AC electric efficiency and efficient heat valorisation by the integrated processes. The project aims at establishing a high volume production of novel tubular proton conducting ceramic cells. The cells will be qualified for pressurized steam electrolysis operation at intermediate temperature (500-700°C). They will be bundled in innovative single engineering units (SEU) encased in tubular steel shells, a modular technology, amenable to various industrial scales. GAMER focuses on designing both system and balance of plant components with the support of advanced modelling and simulation work, flowsheets of integrated processes, combined with robust engineering routes for demonstrating efficient thermal and electrical integration in a 10 kW electrolyser system delivering pure hydrogen at minimum 30 bars outlet pressure.

The consortium covers the full value chain of the hydrogen economy, from cell and SEU manufacturer (CMS), system integrators (MC2, CRI), through researchers (SINTEF, UiO, CSIC), to end users in refineries, oil and gas, chemical industry (CRI, Shell BV International, with advisory board members YARA and AirLiquide). All along the project, these experienced partners will pay particular attention to risk management (technical,economic, logistic, business) and ensure progress of the technology from TRL3 to TRL5. The overall consortium will perform strategic communication with the relevant stakeholders in order to ensure strong exploitation of the project's results.

1.2 The novel tubular SEU

In the GAMER project, we focus on the demonstration of an innovative, low cost and modular hydrogen production technology utilising *tubular proton conducting ceramic cells* and their inherent advantages for steam electrolysis:

- *Scalability and modularity* of the electrolyser system: the electrolyser is designed for scale (small, medium, large)
- *Reduced operation and maintenance costs* compared to planar stack towers: possible to "isolate" one or several SEUs from the system without shutting it done completely; possibility to change some SEUs
- *Reduced risks* in case of leakage due to low volume of SEU
- *Lower operating temperature* (600°C) than SOE reducing degradation associated to cation diffusion, and enabling use of lower cost steel for pressure vessel;
- *Production of pure dry hydrogen* at the anode side, preventing risk of oxidation encountered in SOE;
- *Increased safety*: In PCE, any increase in pH_2O increases the pH_2. In contrast, the SOE must have a high pO_2 alone at one electrode to balance the pH_2O+pH_2 at the opposite electrode. Pure hot high pressure O_2 is risky. Any increase of pH_2O in the SOE leads to a corresponding decrease in available pH_2 at the same pressure.

- *Increased robustness of tubular cells*, in particular, when exposed to pressure differentials compared to planar cells
- *Reduced sealing area* compared to planar cells

This novel design concept has also challenges, which are addressed in GAMER:

- Current collection is challenging compared to planar technology. This is alleviated in GAMER by the use of lower current density cells.

- Lower current density of the cells compared to SOE. This is compensated in GAMER by increased surface area and lower cost of PCE cells.

The tubular cells in GAMER integrate a proton conducting electrolyte based on Y-doped $Ba(Zr,Ce)O_3$ (BZCY). The cells will consist of a porous Ni-BZCY cathode for the H_2 side (also ensuring mechanical strength), a thin dense BZCY-based electrolyte, a porous anode for the H_2O+O_2 side, and a current collector system. They are assembled in a steel pressure vessel enabling safe pressurized operation of at least 30 bars and 700 °C in high steam content.

1.3 Deliverable 3.2

In this report, we refer to the first generation of tubular cells assembled with proprietary sealing technology and state of the art current collection system mounted in a steel vessel. It is emphasized that the actual design of the SEU (including current collection system) to be integrated in the electrolyser system is under patenting action, and will therefore not be detailed here.

This deliverable presents the methodology used for the qualification tests of primary components and assembled parts performed for the construction of the hydrogen generator in GAMER. The type of performed experiments and operating conditions for each component (cells, seals, manifolds, interconnects, vessels) and assemblies (cells+vessel; cells+seals; seals+ interconnects) for qualification testing of key enabling components are defined in D3.1.

For applicability validation of individual components, the main focus has been laid on chemical stability and transport properties under operating conditions. Regarding fully-assembled cells, both mechanical and functional parameters of the components are important.

Results of these experiments are reported in a confidential report, pending the assessment of the patenting action on the SEU design. They will be disseminated at a later stage to the public. Below, we report on a selected amount of results, which are related to the core materials of the cells.

2 Qualification methodology

The project uses as starting point, the tubular cells and components for assembly (seals, interconnects, manifold, feedthroughs and steel vessel) selected by partners (CMS, UiO, SINTEF, CSIC) based on their background knowledge and know-how.

Non-destructive protocols of verification of durability using a set of electrical, electrochemical, mechanical and pressure decay leakage tests in operating conditions are completed by post-testing characterization methods (microscopy and diffraction) following. The qualification tests report here were carried out following the protocols and criteria established in the public deliverable D3.1 in GAMER.

2.1 Transport properties - qualification tests

2.1.1 Internal resistance

Measurement of internal resistance across outer current collector, seal, interconnect, and internal current collector/electrode: measured on assembled unit at room temperature using hand-held multimeter. Sufficient electrical percolation is achieved with resistance values below 1-2 Ω, as considerable contact resistance is expected from the multimeter pins.

2.1.2 Sheet resistance – current collection layer

For validation of materials and processing procedures for current collectors, the sheet is measured on a separate single-cell setup. A four-point measurement setup is employed at both room temperature and at elevated temperatures (400 °C to 700 °C) in air (for positrode) and 5% H_2 (for negatrode).

2.2 High steam stability

To verify that each individual component and assembled parts (e.g. cells + seal; cell+ seal + manifold; interconnect + seal, etc.) can maintain its integrity and functionality in pressurized electrolysis operation stress test under working conditions of individual components has been performed.

Test conditions:

- ✓ Time = 100 h
- ✓ Temperature = 600 °C
- ✓ Pressure = 28 barg (75% steam + 25 oxygen)
- ✓ Gas flow:
    - Steam = 375 Nml/min
    - Oxygen = 125 Nml/min

3 Chemical stability of cell components

In this section, the electrolyte and H_2O-O_2 electrode materials were tested under high-steam pressure. Phase composition of the electrolyte remains unchanged after thermal treatment under high steam pressure conditions. Only small decrease of cell parameter was observed, which is related to the oxygen non-stoichiometry. No variation was observed for the electrode materials. Results of X-ray diffraction studies are given below for these materials.

3.1 Half cell: BCZY27 ($BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$)

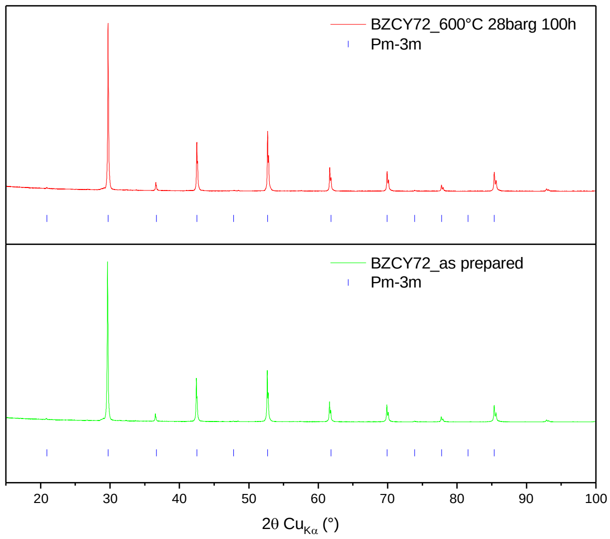

Figure 1 Structural analysis of BCZY after 100h of steam exposure

After the test:
a=b=c=4.253273(26)Å
α=β=γ=90°

As prepared:
a=b=c=4.251193(9)Å
α=β=γ=90°

3.2 Electrode materials

3.2.1 LSM ($La_{0.8}Sr_{0.2}MnO_3$)

- Chemical stability

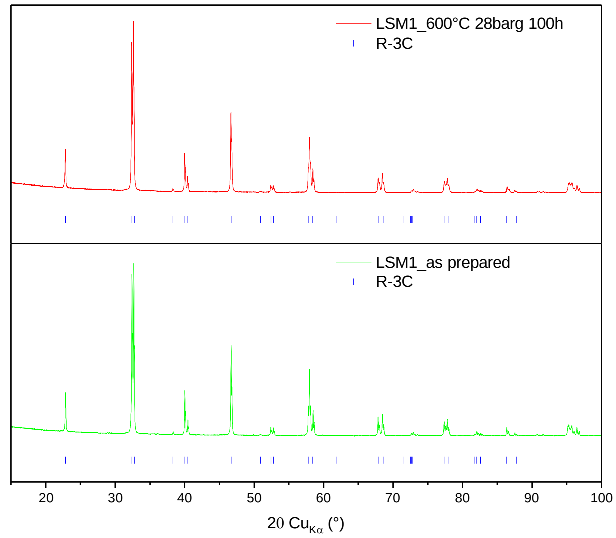

Figure 2 Structural analysis of LSM after 100h of steam exposure

After the test:
a=b=5.5155592(39)Å
c=13.359921(112)Å
α=β=90°
γ=120°

As prepared:
a=b=5.522332(32)Å
c=13.367443(89)Å
α=β=90°
γ=120°

3.2.2 LSCM ($La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_3$)

- Chemical stability

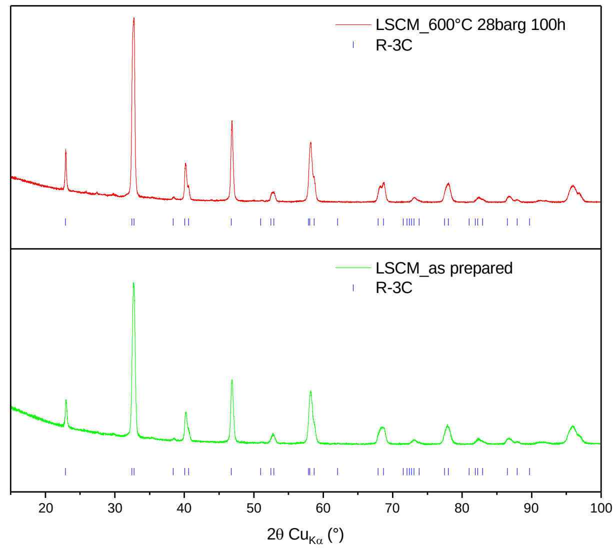

Figure 3 Structural analysis of LSCM after 100h of steam exposure

After the test:
a=b=5.505380(95)Å
c=13.341151(306)Å
α=β=90°
γ=120°

As prepared:
a=b=5.512539(124)Å
c=13.358055(426)Å
α=β=90°
γ=120°

3.2.3 BGLC ($Ba_{0.5}Gd_{0.8}La_{0.7}Co_2O_{6-\delta}$) – delivered by SINTEF

- Chemical stability

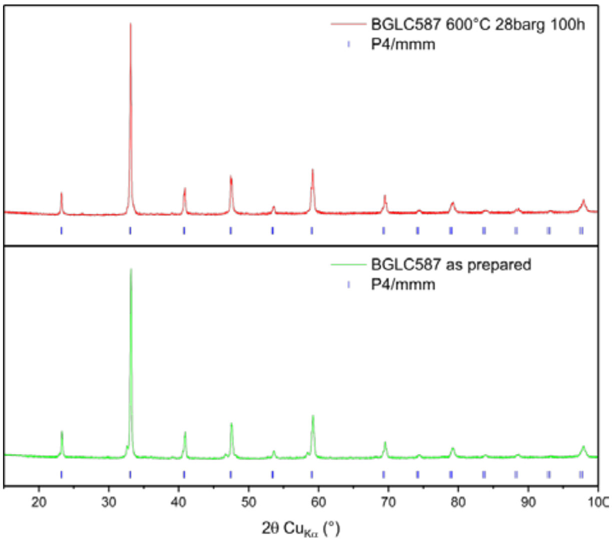

Figure 4 Structural analysis of BGLC after 100h of steam exposure

After the test:
a=b=3.829875(187)Å
c=7.649295(692)Å
α=β=90°
γ=112.199(9)°

As prepared:
a=b=3.832592(6167)Å
c=7.508072(532)Å
α=β=γ=90°

4 Assemblies test

Fully-assembled cells with positrode and current collector, sealed and reduced inner electrode were tested for electrochemical performance in electrolysis. Positrode comprising either a BZCY27 backbone infiltrated with BGLC or a LSM-BZCY composite infiltrated with catalyst. Current collection layer comprised either Au, Ag, oxide or composite mixture.

4.1 Materials validation of components and single cell assembly

A preliminary assessment is a visual inspection of shape, roundness, straightness.

Leak tests were performed in acetone with internal overpressure of 1 bar of helium. For all accepted tubes no visible bubbles were observed and pressure remained unchanged during 1h (Figure 5).

Figure 5 Leak test with acetone

Moreover, in order to optimise glass sealing materials high temperature leak test were performed with helium overpressure, as reported in a previous project (Figure 6).

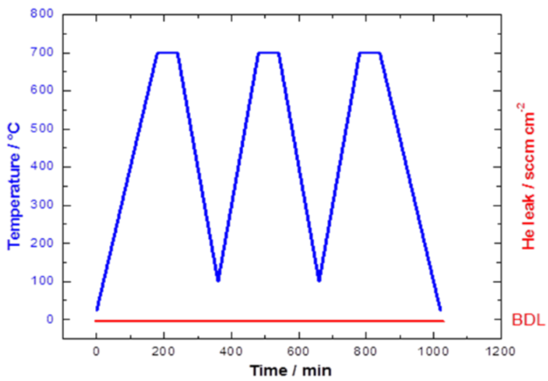

Figure 6 Gas tightness test

4.2 Electrochemical performance test of fully assembled cell

For validation of materials selection and processing procedure of complete single-cell assembly, the cell was reduced, sealed, capped and tested in a single-tube test reactor according process flowsheet defined in D3.1.

Test conditions:

- ✓ Total pressure = 3 barg
  - o pH_2O (positrode) = 1.5 barg
  - o pO_2 (positrode) = 0.1 barg
  - o pAr (positrode) = 1.4 barg
  - o pH_2O (negatrode) = 0.1 barg
  - o pH_2 (negatrode) = 0.5 barg

  - o pAr $_{(negatrode)}$ = 2.4 barg
- ✓ Temperature = 600 °C
- ✓ Voltage = 1.3 V

➢ BGLC-BCZY

A set of 5 cells made from short segments (6 cm length) with a BZCY backbone were reduced and sealed onto an alumina riser. These were then subsequently coated with a BGLC loaded-gel suspension (comprising both calcined oxide and nitrate precursors) before firing in a dual atmosphere setup at temperatures ranging from 900°C to 1000°C (Figure 7).

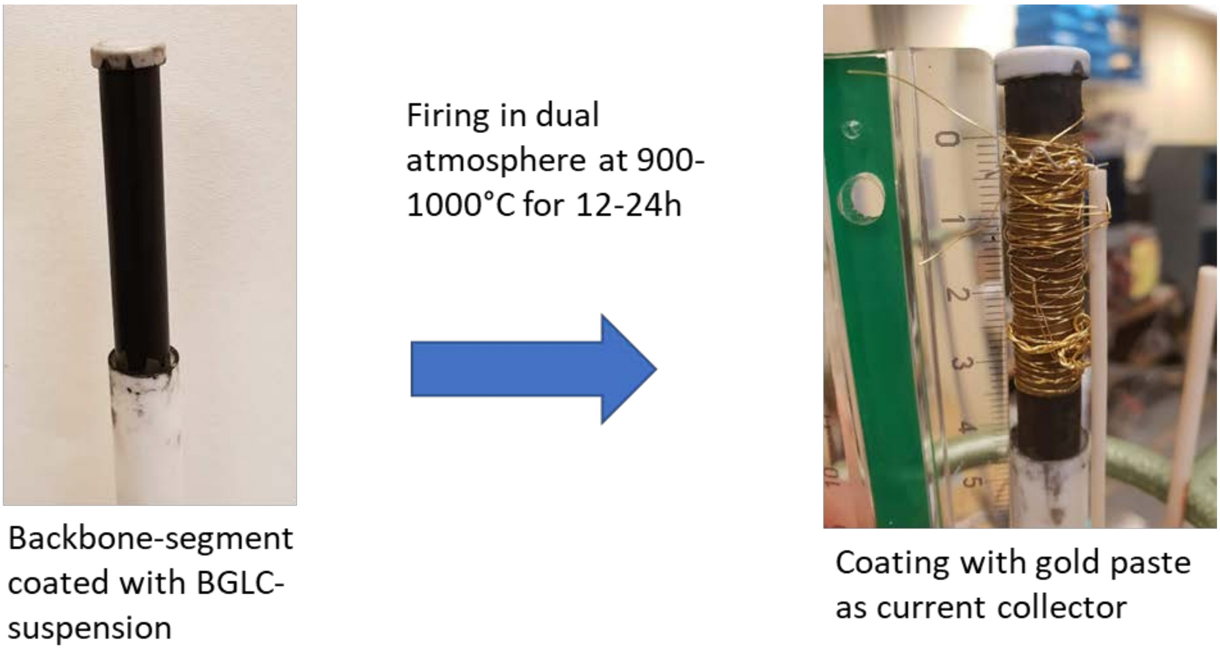

Figure 7 BGLC-BCZY cell preparation

The cells annealed at 1000 °C cracked during the firing procedure due oxygen permeation through the BZCY electrolyte that eventually caused re-oxidation of the Ni-metal at the negatrode-electrolyte interface. At 900 °C and 950 °C, the rate of oxygen permeation is reduced and the cells survived the annealing procedure when using 30% H_2 (30 mLmin^{-1} H_2 and 70 mlmin^{-1} Ar) in the inner sweep gas and 10% O_2 in the outer sweep gas.

The cells were then coated with gold paste using brush painting and wrapped with gold wire as a current collector, before being mounted in a ProboStat measurement cell for electrochemical testing. This setup has a limitation on both current density (2 A total current) and steam partial pressure (maximum 2 bar steam), so the tests were performed under mild conditions initially:

- Temperature: 600 °C
- Positrode gas composition
  - o 1 bar steam
  - o 0.1 bar O_2
  - o 0.9 bar N_2
- Negatrode gas composition

- 0.2 bar H_2
- 0.05 bar steam
- 1.75 bar Ar

The electrochemical performance (a) and impedance at OCV (b) of two cells sintered at 900°C and 950 °C are summarized in Figure 8. As is evident, the cell annealed at higher temperatures displays the highest performance, predominantly due to a lower electrode polarization resistance.

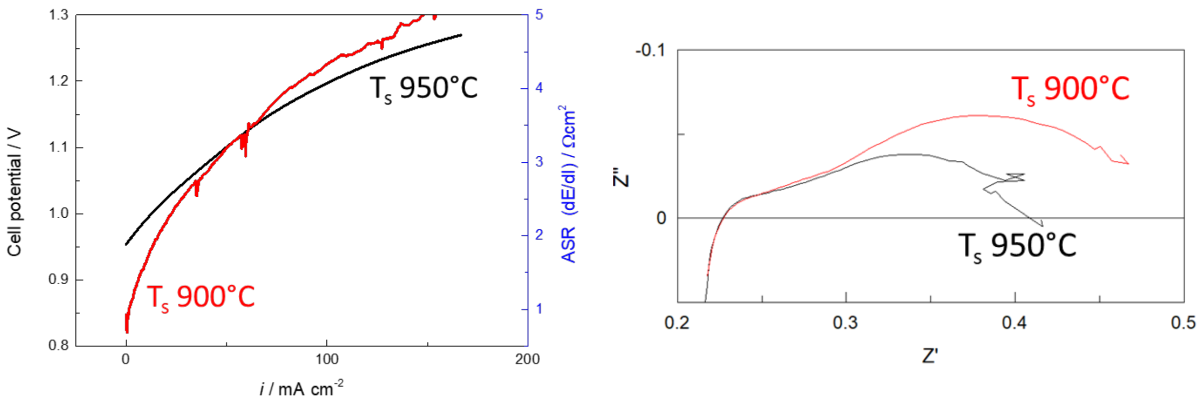

Figure 8 a) IV-curve of two BGLC cells annealed at 900°C and 950°C measured at 600°C in 1 bar steam on the positrode. b) Nyquist plots of the same cells at open-circuit.

The cell annealed at 950 °C is compared to the best results obtained in the ELECTRA project using BGLC-BZCY composite electrodes (including reduction/sealing under bias operation) in Figure 9. As can be seen, the cell annealed at 950°C displays better performance than the ELECTRA cell predominantly due to a lower ohmic resistance. This is primarily attributed to better current collection and an improved experimental setup. Moreover, the EIS data reveal a slightly larger electrode polarization resistance for the GAMER cell. The latter may be attributed to a lower adhesion of the electrode layer resulting in a loss of electrochemically active surface area for the water splitting reaction.

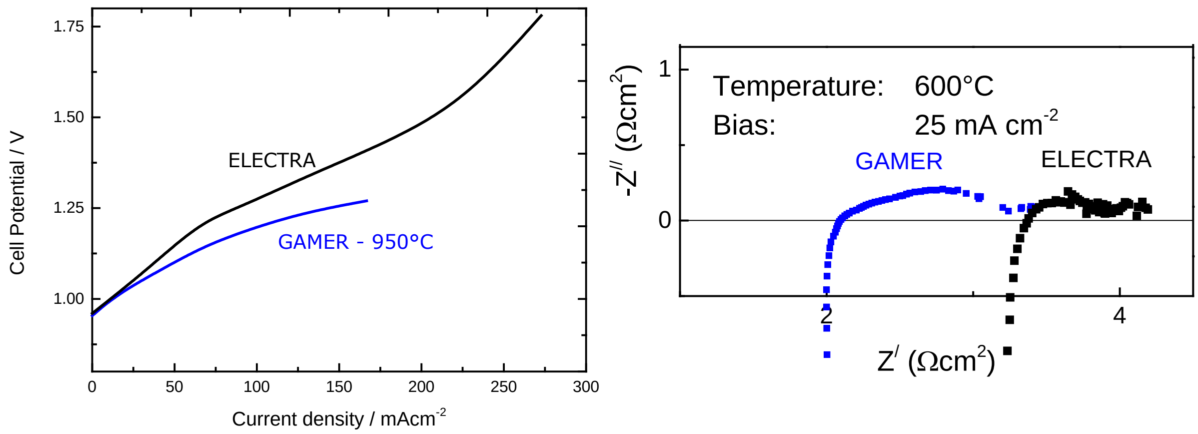

Figure 9 Comparison the best performing BGLC-based cells in GAMER and ELECTRA.

- LSM-BCZY

The electrochemical performance of tube cells prepared according process flowsheet delivered in D3.1 was studied. Gold paste and wire was used a current collector. LSM-BCZY electrode is stable during the half-cell reduction and sealing, and therefore, the manufacturing of the cell becomes simpler and faster. This electrode also requires a final step of catalyst infiltration. The electrode performance under operation, i.e. @50mA·cm^2, exhibits ASR below 200 mΩ·cm^2 (Figure 11 right-hand). Under these conditions, the cell operation is limited by ohmic resistance that can be strongly reduced by appropriate current lead and collection together with electrode contacting, as shown for BGLC-cells (above).

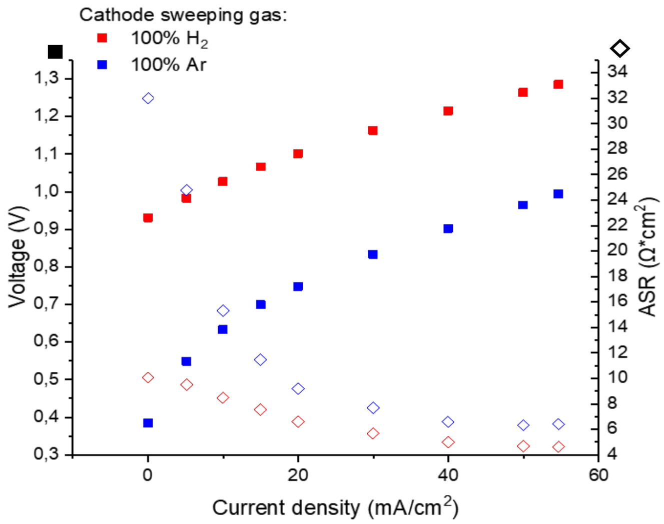

Figure 10 Current-voltage curves and area-specific resistance (ASR) of cell measured at 600 °C under atm. pressure (HS: 50H$_2$ (50Ar), SS: 50Air+50Steam)

Figure 11 LSM-BCZY27-BCZY27Ni60 cell sealed into alumina riser with Gold as current collector

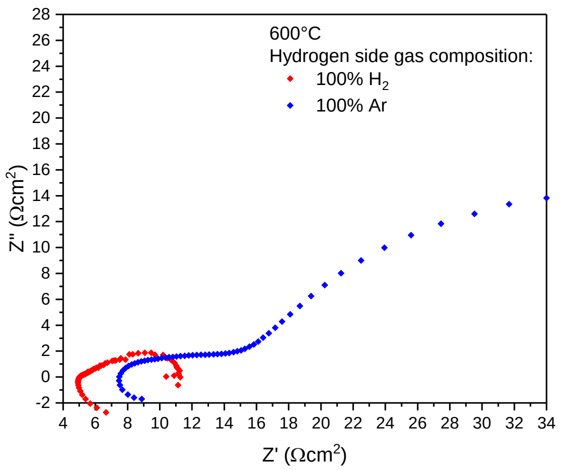

Figure 12 Impedance spectra of T2_11_2017 at 600 °C under atm. pressure without Bias

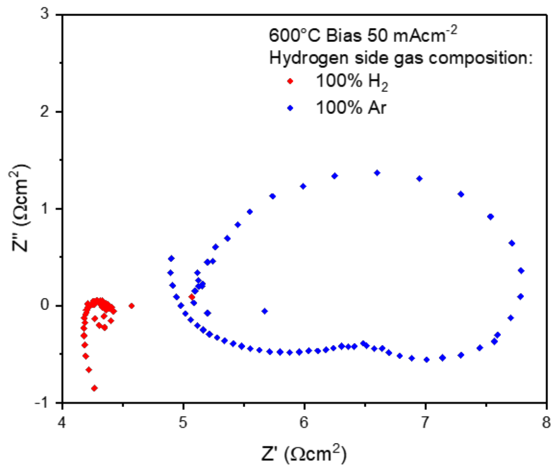

Figure 13 Impedance spectra of T2_11_2017 at 600 °C under atm. pressure 50mAcm^{-2} of Bias

5 Conclusions

Testing of all proposed cell components (electrolyte, positrode, cell constructive parts and current collectors/connectors) in high-pressure steam at 600 °C confirmed good structural stability. The electrochemical tests under electrolysis mode of fully-assembled tubular cells confirms the performance and operability for the cells built following the established manufacturing procedures and cell architecture.

6 References

1. Majewski, A.J., et al., Materials for Renewable and Sustainable Energy, 2018. **7**(3): p. 16.

7 Acknowledgements

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