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Ph.D. Thesis

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Investigation of the stability of oxygen electrode of solid oxide electrolysis cell (SOEC) operated with steam as a sweep gas for simultaneous production of high purity oxygen and hydrogen

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Realizacja opisanych tutaj badań była możliwa dzięki wsparciu i zaangażowaniu wielu wspaniałych osób, z którymi miałem przyjemność współpracować w trakcie mojej dotychczasowej pracy naukowej. Wszystkim im pragnę w tym miejscu podziękować.

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Moim rodzicom...

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Streszczenie

Rozprawa doktorska podejmuje tematykę stabilności pracy stałotlenkowych ogniw elektrochemicznych pracujących w trybie elektrolizy (SOEC). Praca skupia się na weryfikacji możliwości wykorzystania pary wodnej lub strumienia tlenu jako gazu omywającego elektrodę tlenową. Pracę podzielono na 6 głównych rozdziałów.

We wprowadzeniu omówiony został kontekst rosnącej roli wodoru w gospodarce światowej, jego znaczenie w dekarbonizacji przemysłu i transportu oraz strategie wodorowe wdrażane w różnych krajach. Przedstawiono przegląd metod produkcji wodoru, ze szczególnym uwzględnieniem elektrolizy jako niskoemisyjnej alternatywy.

Rozprawę otwiera szeroki przegląd literaturowy, który zawiera opis podstawowych zagadnień związanych z ogniwami SOC jak zasadę działania, termodynamikę procesu elektrolizy czy aspekty materiałowe technologii ogniw stałotlenkowych. W tym rozdziale przedstawione są także bardzo szczegółowo różne przyczyny degradacji jakie mogą wystąpić w ogniwach wysokotemperaturowych z rozdzieleniem na procesy charakterystyczne dla każdej z elektrol i elektrolitu, ze szczególnym akcentem na elektrodę powietrzną, a także specyfikę warunków operacyjnych.

W rozdziale 3 przedstawione zostały szczegółowo techniki badawcze i analityczne wykorzystane w trakcie prac eksperymentalnych. Zagadnienia obejmowały pomiary elektrochemiczne takie jak rejestracja charakterystyk prądowo-napięciowych (I-V), długoczasowe monitorowanie napięcia ogniwa pracującego w trybie galwanostatycznym, a także pomiary oraz analizę wyników spektroskopii impedancyjnej (EIS). W tym rozdziale wyjaśniono również techniki wykorzystywane w analizach post-mortem, gdzie badano zagadnienia związane ze zmianami materiałowymi zachodzącymi w elektrodach ogniwa oraz ich mikrostrukturę. Przedstawiono techniki takie jak skaningowa mikroskopia elektronowa (SEM), analiza pierwiastkowa (EDS) i dyfrakcja rentgenowska (XRD).

Prace eksperymentalne zostały przedstawione w rozdziale 4, gdzie omówiono wyniki badań ogniw SOC w trybie elektrolizy, przy wykorzystaniu różnych gazów omywających: parę wodną, azot i tlen. Prace eksperymentalne obejmowały przygotowanie i adaptację stanowiska badawczego dedykowanego do wykorzystania ogniw SOC o wymiarach 5 cm x 5 cm. W tej części pracy przedstawione zostały wyniki serii krótko- i długoczasowych pomiarów ogniw w różnych warunkach procesowych. Rozdział składa się z 3 podrozdziałów, każdy z nich

poświęcony jest wykorzystaniu innego gazu omywającego. W podrozdziałach omówione zostały szczegółowe wyniki pomiarów elektrochemicznych w tym przebieg zmian napięcia w trakcie pomiarów przy stałym obciążeniu prądowym i towarzyszące im pomiary widm impedancyjnych na różnych etapach pomiaru. W każdym przypadku określana była szybkość degradacji osiągów poszczególnych ogniw. W tym miejscu przedstawione zostały także wyniki pomiarów mikroskopowych i materiałowych zrealizowanych w trakcie analiz post-mortem. Każdy z podrozdziałów kończy się dokładną analizą i interpretacją otrzymanych wyników w formie dyskusji z dostępnymi danymi literaturowymi.

W rozdziale 5 przedstawiona została całościowa dyskusja i porównanie kluczowych wyników degradacyjnych otrzymanych w trakcie kampanii pomiarowej. W rozdziale znalazły się zestawienia wyników i interpretacja rezultatów.

Ostatnią część pracy stanowią wnioski, w którym omówiono konkluzje badań weryfikujących założone hipotezy badawcze. Ponadto zaproponowano kierunki dalszych prac, które mogą przyczynić się do rozwoju dziedziny oraz nowatorskiego podejścia do zastosowania specjalnych gazów omywających.

Słowa kluczowe: SOE, SOC elektroliza wysokotemperaturowa, technologie wodorowe, degradacja

Abstract

The doctoral dissertation addresses the subject of stability of solid oxide electrochemical cells operating in electrolysis mode (SOEC). The work focuses on verifying the possibility of using water vapor or oxygen streams as a sweep gas of the oxygen electrode side. The work is divided into 6 main chapters.

The introduction discusses the context of the growing interest and role of hydrogen in the global economy. Chapter explain the hydrogen importance in the decarbonization of industry and transport, and how this process is supported by hydrogen strategies implemented in various countries. Here an overview of hydrogen production methods is presented, with particular emphasis on electrolysis as a low-emission alternative.

The dissertation starts with a broad literature overview, which describes the field of high temperature electrolysis cell such as the principle of operation, thermodynamics of the electrolysis process, and material aspects of solid oxide cell technology. This chapter also presents in detail various degradation processes that can occur in high-temperature cells. The degradation issues are addressed separately for each electrode and electrolyte, with particular emphasis on the air electrode, as well as the alternative or special operating conditions.

Chapter 3 presents in detail the analytical and testing techniques used during the experimental campaign. This includes electrochemical measurements such as measurements of current-voltage characteristics (I-V), long-term monitoring of the cell voltage under operating conditions in galvanostatic mode, as well as measurements and analysis of impedance spectroscopy (EIS) results. This chapter also presents the techniques used in post-mortem analysis, where issues related to material changes occurring in the cell electrodes and their microstructure were studied by techniques such as scanning electron microscopy (SEM), elemental analysis (EDS) and X-ray diffraction (XRD).

The experimental work is presented in Chapter 4, where the all the results obtained during SOC cell tests in electrolysis mode are discussed. Experimental campaign covered use of various sweep gases such as steam, nitrogen and oxygen. The results were gathered during a series of short- and long-term measurements of cells. The experimental started with the preparation and adaptation of a research test stand dedicated for testing of 5 cm x 5 cm SOC cells. Next the chapter was divided into 3 subchapters, each of which is devoted to the use of a different sweep gas. In the subchapters the detailed results of electrochemical measurements

are discussed, including the evolution of the cell voltage during long-term measurements at a constant current load. At various stages of the cell measurement the impedance spectra were registered and the rate of degradation of individual cell and its performance change was determined. Additionally to the electrochemical results the analysis of microscopic and material changes were carried out during post-mortem measurements. Each subchapter is summed up with a detailed analysis and interpretation of the obtained results in the form of a discussion and comparison to the available literature.

Chapter 5 presents a comprehensive discussion and comparison of key degradation results obtained during the all experimental studies. The chapter is a general discussion and comparison of the data and an interpretation of results.

The last chapter of the dissertation presents the conclusions, in which the outcome of the studies dedicated for verifying the research hypotheses are discussed. In addition, directions for further approach and area of interest have been proposed that may contribute to the development of the field and an innovative approach to the use of alternative sweep gases

Keywords: SOE, SOC high-temperature electrolysis, hydrogen technologies, degradation

List of Symbols

- AEM Anion Exchange Membrane
- ALK alkaline electrolysis
- AMER Americas
- APAC Asia-Pacific
- ASC Anode Supported Cell
- ASG Anode sweep gas
- AUD Australian Dollar
- BL Barrier Layer
- CAPEX capital expenditure
- CFG Cathode Fed Gas
- CL Fuel electrode contact layer
- Co-SOEC Solid Oxide co-Electrolysis Cell
- CSC Cathode Supported Cell
- $CTH_2\;$ Center for Hydrogen Technologies
- DRT Distribution of Relaxation Times
- EDX Energy Dispersive X-Ray
- EIS Electrochemical impedance spectroscopy
- EMEA Europe, the Middle East and Africa
- ESC Electrolyte Supported Cell
- FE Fuel Electrode
- FL Fuel electrode functional layer
- FS Fuel electrode support

GDC or CGO -Gadolinium doped ceria

- IEN Institute of Power Engineering
- IRENA International Renewable Energy Agency (IRENA)
- ISC Inert Supported Cell
- I-V Current-voltage curve
- LSC Lanthanum strontium Cobaltite,
- LSCF Lanthanum Strontium Cobalt Ferrite
- LSCM Lanthanum Strontium Cobalt Manganite
- LSM Lanthanum strontium manganite,
- MIEC -Mixed Ionic Electric Conductors
- MSC Metal Supported Cell
- OCV Open Circuit Voltage
- OE Oxygen Electrode
- **OPEX** operating expenditures
- PE primary electrons in electron microscope
- PEM proton exchange membranes
- PID Proportional integral derivative controller
- PSA Pressure Swing Adsorption
- RE Renewable Energy
- RES Renewable Energy Sources
- S/C Steam to Carbon Ratio
- SDC Samaria-doped ceria
- SE secondary electrons
- SEM Scanning Electron Microscopy

- SMR Steam Methane Reforming
- SOC Solid Oxide Cell
- SOE Solid Oxide Electrolyzer
- SOEC Solid Oxide Electrolysis Cell
- SOFC Solid Oxide Fuel Cell
- SOFEC Solid Oxide Fuel Assisted Electrolysis Cell
- TEC Thermal expansion coefficient
- TPB triple-phase boundary
- USD United States dollar
- XRD x-ray diffraction
- YSZ Yttria stabilized zirconia

$$\sigma_{ion}$$
 - ionic conductivity [S cm⁻¹]

 E_A - effective activation energy of vacancy migration [kJ mol⁻¹]

 $a_{H_2}, a_{O_2}, a_{H_2O}$ -reactants activities

- φ phase shift [rad]
- μ_V mobility of the oxygen vacancies [cm² V⁻¹ s⁻¹]
- μ_o preexponential factor of the vacancy mobility

A - active cell area [cm²]

- ASR Area specific resistance [Ω cm²]
- F Faraday's constant 96 485 C mol⁻¹]
- ΔG Gibbs free energy [kJ mol⁻¹]
- ΔH enthalpy of formation [kJ mol⁻¹]

 ΔH_{vap} - heat of vaporization of water [41 kJ mol⁻¹] - current density [A cm⁻²] i Ι - electric current [A] - imaginary unit or unit imaginary number equal to $\sqrt{(-1)}$ i - universal gas constant [8.314 J mol⁻¹ K⁻¹] R -polarization resistance [Ω cm²] R_p - Ohmic resistance [Ω cm²] R_{Ω} Т - temperature [K] Uact - activation polarization [V] - concentration polarization[V] Ucon - ohmic polarization [V] U_{ohm} - reference voltage from the linear part of the i-v curve for ASR calculations [V] Uref Urev - reversible cell voltage [V] U_{th} - thermoneutral voltage [V] - concentration of oxygen vacancies in the crystalline lattice [cm⁻³] $[V_{0}^{"}]$ Ζ - Impedance - number of electrical charges transferred in the reaction Z

 Z_0 - impedance magnitude [Ω]

 Z_{real} , $Z_{imag}\text{-}$ real and imaginary part of impedance $[\Omega]$

1. Introduction

1.1 Hydrogen economy

The rapid increase of the penetration of renewable energy sources (RES) followed by continuously reduced costs of renewable energy in the last years has created the opportunity for significant progress in the development of green hydrogen technologies. The process of shifting towards low-carbon energy sources is observed in many regions worldwide. In this process hydrogen is seen as a future fuel and substrate, which is often named as a solution to the issues related to the depletion of fossil fuels, and growing problem of global warming. Hydrogen is widely used as a feedstock in various industrial processes: (i) crude oil refining, (ii) ammonia synthesis (fertilizers production), (iii) methanol production, (iv) food processing, (v) plastic industry, and other. Hydrogen is the most abundant element which is available in large quantities but is bonded in various substances. It does not exist naturally in a free form. This is about to change soon as the interest in hydrogen is accelerating. Renewable electricity producers, energy and gas suppliers, automotive industry, oil and gas companies, large engineering companies and most governments of the world's largest economies are interested in hydrogen.

Numerous studies on hydrogen, including national strategies and international road maps, predict a huge increase demand for hydrogen worldwide in the coming years, and in parallel increase of H₂ production capacity. The biggest economies in the world recognized hydrogen and have already developed detailed plans and strategies considering possible implementations and directions of development of hydrogen technologies. Japan was one of the first countries which introduced its hydrogen strategy in 2017 [1] and provided the targets with a general view for the public and private sector. Two years later Japan prepared the strategic road map for hydrogen and fuel cells [2] in which they see water electrolysis for hydrogen production as a one of the development directions. In 2019 South Korea also announced the Hydrogen Economy Roadmap [3] with a goal to make Korea one of the leading hydrogen economies focusing on hydrogen vehicles and fuel cells technology. To support that announcement Korean National Assembly in 2020 has prepared Hydrogen Law in order to create legal framework for the realization of the Hydrogen Economy. In the same year Australia has published their own national hydrogen strategy [4] where Australia's clean hydrogen potential is recognized and various scenarios for Australia as hydrogen producer and exporter are analyzed. Australia also set an ambitious target for reduction of hydrogen production cost below 2 AUD/kg of hydrogen [5]. Since then Australia is year by year moving towards this goal.

The high interest in Asian region has influenced the decisions in Europe which started announcing their strategy in 2020. Netherlands did this in April [6], Dutch government identified goal for 2050 to have 30-50% of final energy consumption realized by hydrogen and biogas. Norway in June 2020 presented National Policy Paper [7] where focus is put on the use hydrogen in maritime sector. Later that year a joint project between Denmark and Norway has been announced within this project, a world largest hydrogen-fueled ferry will be built and will start operation on Copenhagen-Oslo route by 2027 [8]. Also, in June 2020 Germany presented the national hydrogen strategy [9] in which they anticipate that the green hydrogen demand in 2030 will reach 90-110 TWh. In order to fulfil requirements Germany has to increase the installed capacity of electrolyzer up to 5 GW by 2030 and additional 5 GW by 2035.

In July 2020 European Commission set a vision of "installing at least 6 GW of renewable hydrogen electrolyzers in the EU by 2024 and 40 GW of renewable hydrogen electrolyzers by 2030" [10]. Later, in 2020 a France [11] and Spain [12] also presented their vison on hydrogen need and declared targets to install 6,5 GW and 4 GW of electrolyzer capacity by 2030, respectively. In France carbon-free hydrogen could be produced with a use of nuclear electricity. Also, Poland has published at first a draft of Polish Hydrogen Strategy for public

consultation in January 2021. Final strategy has been accepted in November 2021 by Council of Ministers. The strategy sets very ambitious plans to build 2 GW of electrolyzers by 2030, and want to focus on development of domestic hydrogen technologies [13]. Additionally, an agreement between companies, universities, and representatives from various sectors—the first of its kind in Europe—was signed to support the strategy's implementation. The strategy is currently under review, with an update planned for 2025.

Given the long-term nature of these strategies, it seems that the coming years will see enormous growth and development in hydrogen technologies. According to these plans, targets and strategies, hydrogen will become a key factor enabling the massive penetration of renewable energy sources in energy systems, decarbonization of industry and transport [14]. Green hydrogen might be used as a feedstock for green ammonia and green methanol production. Additionally, blending hydrogen into existing gas grid is believed to be the answer for decarbonization of natural gas [15,16]. In geopolitical context hydrogen plays an important role in energy distribution across the different countries and regions. Some countries like Chile aims to become clean hydrogen exporters. Chile ambition in their strategy is to became one of three world's largest hydrogen exporters by 2040 [17] that will satisfy the hydrogen demand around the globe (Chile goal is to turn down production costs to $\$1.50/kg H_2$ by 2030).

All this strategies and plans show the tremendous interest in green hydrogen technologies. While in 2017 only Japan had their hydrogen strategy, today it is more than 30 countries that are involved and want to take part in the hydrogen economy. The plans are followed by financial support. According to IRENA in 2021 governments allocated 65 billion USD support for development of clean hydrogen technologies (Germany, France, and Japan are leaders in this commitment) [18]. Hydrogen Council predicts that by 2050 the development of the hydrogen market and hydrogen technologies in the world will stimulate the creation of 30 million new jobs [19]. Almost 25 GW of electrolyzer capacity was planned to be installed by industry sector before 2026 [20] and up to 160 billion USD is already invested in frames of the announced hydrogen projects due 2030 (**Figure 1**). However the progress is somehow slower and it is estimated that in 2024 the installed capacity of electrolyzers reached 5.2 GW, what is still a 9 times growth since 2021 [21].



Figure 1. Green hydrogen installation, projects and infrastructure [18]

Despite the growing interest in green hydrogen technologies, at the moment most of the global production of hydrogen in based on the conversion of fossil fuels (95% of the global hydrogen supply). The leading hydrogen production technologies are natural gas with methane reforming (SMR), cracking of oil products in refining processes or coal gasification (mostly China).

The use of natural gas and its decomposition via steam methane reforming makes 48% of industrial hydrogen production today. This is due to the fact that this process and technology is mature and most cost effective (but strongly depends on the gas prices).

However, there is an alternative that was rediscovered, a different route for hydrogen production - electrolysis. When hydrogen is produced in the electrolysis process realized with a use of renewable energy sources such as wind, photovoltaic, biomass, hydrogen obtained in this manner is then considered as a renewable fuel (low-/zero- emission hydrogen). The falling prices of renewable electricity and growing penetrations of RES allows electrolysis technologies to become more competitive at the hydrogen market.

1.2 Water electrolysis

The general principles of electrolysis are very simple. The process relies on supplying DC electrical power which is delivered to two electrodes immersed in water. In this electrochemical process water is decomposed into hydrogen and oxygen which are released on cathode and anode, respectively. The gases can be easily separated. The efficiency of electrolysis can be boosted by introduction of highly-active catalytic electrodes. Generation of hydrogen from water during electrolysis is a clean technology and it is considered as an environment friendly (especially when integrated with RES), as it is not generating any pollutants (such as dust, chemicals). This condition is satisfied provided the electricity is supplied from zero-emission sources, such as renewables or nuclear.

The electrolysis of water used to be a relevant method for hydrogen production (in 50's and 60's), but because of fast development of fossil fuels based methods, which are much cheaper, electrolysis has been replaced, and now constitute only minor share (5%) of the overall hydrogen production. Additionally, the production of green hydrogen (based on RES) via water electrolysis contributes to less than 0.02% of today's global hydrogen production [20]. Electrolysis is commonly used where high purity hydrogen is required. Additionally, among all hydrogen production technologies, water electrolysis is perceived as the technology with the higher potential for the reduction of cost of hydrogen production in the near future comparing to other methods [22] and with growing of manufacturing capacities (**Figure 2**).



Figure 2. Electrolyzers manufacturing capacity, based on the investment plans AMER = Americas; APAC = Asia-Pacific; EMEA = Europe, the Middle East and Africa. [18]

There are four generic types of electrolyzers which are considered to play a key role in growth of hydrogen Economy. Alkaline electrolysis (ALK), electrolyzers with an electrolyte based on Proton Exchange Membrane (PEM), Solid Oxide Electrolyzer (SOE), and Anion Exchange Membrane (AEM). ALK and PEM are already commercially available, and SOE and AEM are in early stage of commercialization. Currently, the most commonly used technology is the alkaline electrolysis, which despite the several disadvantages and low gas purity, has achieved the highest technological maturity. The production cost and efficiency of different electrolyzers are not the same, but it is expected that the difference in costs and performances will go down as presented in **Figure 3**.

	2020			2050				
	ALK	PEM	AEM	SOE	ALK	PEM	AEM	SOE
Cell pressure [bar]	< 30	< 70	< 35	< 10	> 70	> 70	> 70	> 20
Efficiency (system) [kWh/kgH ₂]	50-78	50-83	57-69	45-55	< 45	< 45	< 45	< 40
Lifetime [kh]	60	50-80	> 5	< 20	100	100-120	100	80
Capital costs (stack-only) [USD/kW _{el}]	270	400	-	>2000	< 100	< 100	< 100	< 200
Capital cost range estimate for the entire system > 10MW [USD/kW _{el}]	500-1000	700-1400	-	-	< 200	< 200	< 200	< 300

Figure 3. Comparison of various technologies of electrolyzers [20]

Despite that only a limited range of commercial products for hydrogen production based on solid oxide cells (SOC) are available at this stage, even that the SOE technology is the most efficient amongst other [23]. The basic concept, materials, and solutions are developed based on experience with SOC operating in the fuel cell mode (Solid Oxide Fuel Cells, SOFC) [24], but apart from that SOE has been proven by development and operation of short stacks, and small scale electrolysis systems (e.g. Sunfire Hylink 150 kW_{el} system for Green Industrial Hydrogen project) [25]. SOEs are currently the subject of development and implementation in research projects, as well as integration with the industry (e.g. Sunfire-HyLink in the production of Salzgitter steel or multi-MW electrolyzer for the needs of the Neste Bio-refinery in Rotterdam). In May 2021, Sunfire announced the successful testing of its 2nd generation SOE 225 kW electrolyzer [26].

The Institute of Power Engineering – National Research Institute in Poland is also one of the leaders and developers of this technology. We were involved in several project where we successfully delivered hydrogen systems to Polish companies positioned in the gas&oil&energy sector. [27, 28, 29]. In VETNI project we designed and operated the 30 kW electrolyzer unit supplied with technical steam from refinery infrastructure in Jasło (**Figure 4**).



Figure 4. The 30 kW SOE electrolyzer system integrated in Jasło

System is able to produce 16 kg H₂ daily. Additionally we delivered the rSOC system and connect it with BB25p biomass unit in the Elbląg Combined Heat and Power Plant (Energa Grupa Orlen). Here the goal was to test and analyze the concept of reversible system which in moments of electricity overproduction can consume steam and electricity from the biomass unit and produce hydrogen, while in times of high electricity demand it can consume stored hydrogen and generate additional electricity.

1.3 Motivation

The primary function of solid oxide electrolyzers is the efficient production of hydrogen. The high operating temperature (in range of 650-850 °C, depending of the SOE type) and catalytic properties on the fuel electrode enables also operation in various modes like CO₂ electrolysis, co-electrolysis (electrolysis of steam and CO₂ mixture), or direct-methanation. In these modes hydrogen is produced along with other fuels such as carbon monoxide, syngas or methane. This is a great advantage to simultaneously produce hydrogen and/or other fuel gases in one system since it may have a big impact to the final economic result of the system and possible integration routes with other processes and application in the industry. The topic is very promising and this path of SOE operation is being widely researched. On the other hand, during the electrolysis process there is an unavoidable parallel production of oxygen happening on the in the same system. In SOE when water molecule is split, hydrogen is produced on the cathode electrode, while the oxygen is transferred through the electrolyte and released on the anode side. The most common realization is the collecting of oxygen by Anode Sweep Gas (ASG) usually air. Air is cheap and easy available gas, but the use of air as a extractor leads to the dilution of pure oxygen produced in SOE with nitrogen. An O₂-enriched air in some specific integration cases might be used onsite, but the most common approach is to release the gas to the atmosphere. The sweep gas in the SOE system has important additional function to maintain the thermal balance of the electrolyzer, so it is not easy to just cease of air delivery for pure oxygen recovery. Yet if the air could be substituted by different sweep gas that will allow easy oxygen separation the possibility of parallel production of pure hydrogen and pure oxygen in the same system can be accomplished. Steam has been proposed as an alternative sweep gas since it is already present in the electrolyzer system and allows separation of oxygen via condensation of the water from the gas exiting the anodic compartment of an electrolyzer. The change of the sweep gas from air to steam will led to decrease of oxygen concentration in anodic compartment what may have a positive impact on the efficiency of hydrogen production.

Nowadays the oxygen production is realized either by pressure swing adsorption PSA (maximum $95\% O_2$) or a in large industrial scale by cryogenic separation process. Both of these processes are considered as a high energy consumption processes, causing increase the pure oxygen price. In this context, the production of oxygen as a by-product during steam electrolysis is an interesting, but still not fully recognized route in both, the developing electrolyzer market and in the scientific domain. The operation of SOE with steam as a sweep gas in the anode side is poorly researched and in particular the aspect of the stability of the oxygen electrode has not

been investigated so far. The harsh environment with changing oxygen content and humidity might be a challenge for the material durability and performance, but the first step into the subject has to be taken and the problems and opportunities has to be identified to allow further development of the efficient and cost-effective hydrogen production.

1.4 Objectives of the thesis

The key hypothesis of this thesis is that the use of steam as a sweep gas in the anodic compartment of SOE (oxygen electrode) should allow easy and efficient extraction of high purity oxygen (**Figure 5**). Application of steam as a sweep gas will allow easy oxygen recovery (by simple process based on condensation of steam). A stable oxygen electrode which can maintain its performance in pure steam can offer a completely new route for simultaneous production of hydrogen and oxygen. Moreover, this can make the high temperature electrolysis process more efficient and economically viable due to the valorization of by-product oxygen [30]. Finally, such an approach might foster the integration of high temperature electrolyzers with conventional power systems, enabling efficient transition to oxy-combustion of fossil fuels.





The scientific goal will be experimental validation of high temperature electrolysis under the conditions when steam is being supplied to the both sides of the electrolytic cell, with simultaneous generation of oxygen and hydrogen. Lanthanum Strontium Cobaltite Ferrite (LSCF) is one of the most commonly used material for oxygen electrode in SOEC and can withstand small content of steam in process gas, e.g. humidified air. It is expected, that LSCF-based electrode layer can demonstrate sufficient stability in steam flow while operating as

anode of the SOC. In this work a pure steam will be used to validate the stability of the oxygen electrode. The hypothesis will be verified on the basis of the following sub-tasks:

- 1. Study of the degradation effect in electrolysis cell related to the use of steam as anode sweep gas including long-term electrochemical measurements.
- 2. Influence of the anodic polarization combined with extreme humidity on the LSCF electrode material microstructure and stability.

Simultaneous pure hydrogen and oxygen production in high temperature electrolyzer can also be achieved by the oxygen recirculation in the anodic compartment. Since the process can be simulated by simple operation with oxygen as a sweep gas a **secondary hypothesis** will be proven: **for the solid oxide cell in the electrolysis mode usage of the pure oxygen as anode sweep gas can have sufficient impact on the stability of the LSCF electrode layer.**

2. Literature overview

2.1 History of solid oxide electrolysis

The idea to exploit solid oxide cells for steam electrolysis in not a new concept. Early stage of the development of SOE took place in 70s and 80s of the 20th century when it was used in the space programs [31]. The main application goal was to regenerate the oxygen from respiratory carbon dioxide and water during space flights. The key advantages offered by SOE at that time were the following:

- water and CO₂ can be decomposed in the same cell,
- oxygen required no purification (only impurities such as CO₂ and H₂O which were acceptable),
- no problems with zero gravity (no liquid phase),
- low physical weight small and compact system (low gravimetric and volumetric power density).

Later, in 1981, Isenberg demonstrated operation of SOE lasting 5,000 h and the possibility of thermal cycling of the SOE stack [32]. Later he also analyzed the possibility of simultaneous electrolysis of steam an carbon dioxide in high temperature electrolysis process [33-34] for recovery in life support systems. Solid oxide cells has been further researched by Dönitz and Erdle in 90s [35-36]. They were focusing their work on electrolyte supported tubular SOC and have performed long-term (1,000 h) single cells test at 1,000 °C and current density 0.3 A/cm². Corresponding electrical energy consumption was 2.6 kWh/Nm³. During their work, team also managed to integrate SOC into larger electrolyzer modules that consisted of ten tubular cells (**Figure 6**).



Figure 6. SOC module concept by Donitz [35] and full scale steam electrolyzer [37]

The obtained by them results demonstrated that high-temperature electrolysis of steam may be an promising alternative for hydrogen production offering good efficiency and having the potential for implementation in fuel refining industry.

Due to the fact that the performance of cells at that time was rather poor and materials were very expensive the electrolysis based on SOC has been not been a subject for research for next couple of years. In 1994 Plazak [37] pointed out the two biggest problems that were the issue with further development of SOC for electrolysis: material issues, fabrication problems that are related to the extreme temperatures (cells were operated around 1000 °C at that time). He stated that practical use of SOE was at this point irrelevant. From that moment the scientific effort has been shifted almost completely to the complementary technology of solid oxide fuel cells which fast development at the early 2000 resulted in enormous progress in new materials discovery and fabrication methods. Access to new materials and extensive experience with SOFC once again opened the electrolysis potential and allowed re-activation of the research on solid oxide electrolyzes technology (**Figure 7**).



Figure 7. Number of research articles identified in Scopus using phrase "Solid oxide electrolysis". [38]

Also, the Institute of Power Engineering – National Research Institute (IPE-NRI) took this path of technology development and focused its interest on solid oxide electrolyzers in 2017 [39]. The research involved modelling of the cells and systems [40, 41, 42], as well as design and construction of electrolysis systems [28]. The development of the high temperature electrolysis technology in the IPE-NRI was also based on its previous works in field of solid oxide fuel cells [43] [44] [45].

2.2 Principles of SOC operation

High temperature solid oxide cells are the electrochemical devices which consist of three main components: two porous electrodes separated by the electrolyte (oxygen ion conductor). In general solid oxide cell can be operated in two basic modes: as fuel cell for electricity production or as an electrolyzer cell for hydrogen production.

The principles of operation and the electrode reactions of SOFC and SOEC has been presented in **Figure 8**, **Table 1** and **Table 2**. Basically, in the case of SOFC the electricity is generated in the electrochemical reaction in which fuel (i.e. hydrogen, methane, carbon monoxide, ammonia) is oxidized by oxygen ions transported through the electrolyte. The air is delivered to the oxygen electrode (cathode) and at cathode/electrolyte interface oxygen molecules are reduced into of oxygen ions which are conducted through electrolyte to the fuel electrode (anode) due to the gradient of oxygen chemical potential that exist between electrodes (respectively high and low oxygen partial pressure).



Figure 8. Principle of operation of SOC cells in various modes a) Solid Oxide Fuel Cell (SOFC) ; b) –Solid Oxide Electrolysis Cell (SOEC); c) Co-Electrolysis in Solid Oxide Electrolysis Cell (Co-SOEC); d) Assisted Electrolysis (SOFEC)

Table 1. SOFC electrode reactions

Anode reactions:		Overall SOFC reactions:	
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	(Eq. 1)	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	(Eq. 5)
$\rm CO + O^{2-} \rightarrow \rm CO_2 + 2e^{-}$	(Eq. 2)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	(Eq. 6)
$CH_4 + 4O^{2-} \rightarrow H_2O + 8e^{-}$	(Eq. 3)	$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$	(Eq. 7)
Cathode reactions:			
$^{1/2}O_2 + 2e^- \rightarrow O^{2-}$	(Eq. 4)		

Table 2. SOEC/SOFEC electrode reactions

Anode reactions:		Overall SOEC and co-SOEC
SOEC $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^{-}$	(Eq. 8)	reactions:
SOFEC $\frac{1}{4}CH_4 + O^{2-} \rightarrow \frac{1}{2}H_2O + \frac{1}{4}CO_2 + 2e^{-}$	(Eq. 9)	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$ (Eq. 13)
		$CO_2 \rightarrow CO + \frac{1}{2}O_2$ (Eq. 14)
		-
Cathode reactions:		
$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	(Eq. 10)	
$CO_2 + 2e^- \rightarrow CO + O^{2-}$	(Eq. 11)	
$H_2 + CO_2 \rightarrow H_2O + CO$	(Eq. 12)	

During operation of SOEC, electricity has to be provided from an external source to drive the steam and/or CO₂ electrolysis [46]. Steam or carbon dioxide (in case of co-electrolysis) simultaneously undergo the electrochemical reduction on the cathode side (fuel electrode) of the cell. During this reduction H₂ and/or CO are produced respectively as well as O^{2-} . Oxygen is transported in form of oxygen ions through the oxygen-ion conducting electrolyte to the anode compartment where it recombines, and oxygen gas is released. In general, in the most common approach, air is used to sweep oxygen from the electrode. This however is not always the case. In this work the steam is proposed to be used as a sweep gas in order to allow easy oxygen recovery, but also, different possibilities are considered in SOC technology. For example, in order to lower electricity consumption of hydrogen production there is possible operation of SOC in the fuel-assisted electrolysis mode (SOFEC) [47, 48]. In this case air is replaced by a low-cost fuel mixture (carbon, natural gas or biomass) which is introduced and

oxidized in the anodic compartments. This lowers the operating voltage, and significantly decrease the energy required to drive the hydrogen production. In [49] a description and analysis of a new high-efficiency natural gas assisted steam electrolyzer was presented. Natural gas consumes the oxygen produced during electrolysis, reducing the chemical potential in the electrolyzer, thus minimizing electricity consumption. Single-cell experiments have shown a voltage drop of up to 1 V compared to the conventional steam electrolyzer. Additionally, the system analysis shown that the integration of the electrolyzer in the heat recovery system resulted in a highly efficient hydrogen production system (40% raise in comparison to the conventional one).

2.3 Thermodynamics of SOC

The overall energy demand that is consumed during splitting of H_2O molecule is related to the enthalpy of H_2O formation ΔH :

$$\Delta H = \Delta G + \Delta Q \tag{Eq. 15}$$

We can see that the total energy that is needed for the reaction to take place is partially supplied in form of heat ΔQ another fraction constitute electrical energy which is represented by the change in Gibbs free energy ΔG . **Figure 9** shows the temperature dependency of the energy demand and each of the components. Although the total energy demand is rising very slightly with the temperature, the shares of the electrical energy needs and thermal contributions is changing significantly. This opens the possibility for heat integration at higher temperatures.



Figure 9. The temperature dependency of the water electrolysis energy demand [50]

If heat integration is not realized in the system and overall energy demand is realized by electrical energy the minimum cell voltage that is needed for electrolysis to take place is called thermoneutral voltage and is described as:

$$U_{th} = \frac{\Delta H}{zF} \tag{Eq. 16}$$

The z is the number of electrical charges transferred in the reaction (z = 2) and F represents the Faraday's constant (96 485 C/mol). If water is evaporated externally (case of high temperature electrolysis cells) the value of thermoneutral voltage is in range of 1.26-1.29 V. If water is supplied as a liquid (<100 °C) the value grows to approx. 1.48 V. This is because there is an additional heat demand related to heat of vaporization of water ΔH_{vap} (41 kJ/mol). If water is delivered as a liquid (which is the case for low temperature electrolysis systems) the electrolyzer energy demand is rising due to need for vaporization of water during reaction. In high temperature electrolysis systems water is vaporized outside of the electrolyzer and vaporization can be realized e.g. by waste heat instead of high value electrical energy.

If the demand for heat for electrolysis reaction is covered by an external source the reversible cell voltage is related to the change in Gibbs free energy ΔG of the electrolysis reaction via:

$$U_{rev} = \frac{\Delta G}{z F} \tag{Eq. 17}$$

Since the ΔG strongly depends on temperature and pressure of reactants and products:

$$\Delta G = \Delta G^0 + RT \ln K \tag{Eq. 18}$$

Where R stands for universal gas constant, T is temperature in Kelvins, and K is expressed by activity of the reactants a:

$$K = \frac{a_{H_2} (a_{O_2})^{1/2}}{a_{H_2 O}}$$
(Eq. 19)

In summary the theoretical reversible cell voltage can be represented by Nernst equation:

$$U_{rev} = U^0 + \frac{RT}{z F} \ln \frac{p_{H_2} p_{O_2}^{-1/2}}{p_{H_2 O}}$$
(Eq. 20)

For ideal gas:

$$U^0 = \frac{\Delta G^0}{z F} \tag{Eq. 21}$$

The value of the ideal reversible voltage U_{rev} drops from 1.25 V at 0 °C to 0.91 V at 1000 °C. However, the actual cell voltage during operation is higher than the reversible voltage due to the internal losses resulting in additional overvoltage's (also called polarization). The voltage increase is caused by cell resistance and is related to the amount of applied current but also cell geometry, material defects and microstructures of cell components.

The cell potential can be expressed as a sum of four parameters: reversible voltage and three overvoltage's

$$U = U_{rev} + U_{act} + U_{ohm} + U_{con}$$
(Eq. 22)

Where U_{act} is activation polarization, U_{ohm} is ohmic polarization and U_{con} is concentration polarization. The activation and concentration polarization have a non-linear characteristic on i-v curve while ohmic loses increase linearly with current (Figure 10)



Figure 10. Cell voltage and various overpotentials in electrolysis mode.

2.3.1 Activation Polarization

The activation polarization or overpotential is associated with the losses related to the electrode processes. The reactions that are taking place at the cell electrodes requires some minimum amount of energy for activation. The slow reaction kinetics may result in resistance and need for additional voltage to overcome the activation barrier. Therefore higher temperature and good catalytic properties of the electrode material are desired and may help to limit activation loses. The activation polarization is mainly relevant at low current densities.

2.3.2 Ohmic losses

The ohmic polarization is related to the ionic resistivity of the electrolyte, ohmic resistance of the electrode martials but also to the contact resistance between cell components, interconnects, contact layers, and other. Cell geometry (microstructure and various layers thicknesses), materials choice and operating temperature are the most important parameters that influence the ohmic loses. In solid oxide cells the ionic resistance of the electrolyte is usually the main source of the resistance therefore thinner electrolyte is preferred and electrode supported cells are usually adopted especially at moderate temperatures. Overall ohmic loses are proportional to the applied current.

$$U_{ohm} = \frac{I}{A} \times ASR \tag{Eq. 23}$$

Where I represents current [A], ASR is the area specific resistance [Ohm cm²] and A is the active cell area [cm²]. Area specific resistance represents the combined resistances of all loss mechanisms that are taking place in the cell and is commonly used to compare the basic performance of various cells. ASR can be calculated as:

$$ASR = \frac{U - U_{ref}}{i}$$
(Eq. 24)

Where i is current density $[A/cm^2]$ and U_{ref} is the reference voltage from the linear part of the i-v curve.

2.3.3 Concentration Polarization

Concentration loses arise from the limits of gas diffusion and the high level of steam conversion. The polarization related to gas diffusion occurs when the products and reactants of the electrode processes are not transferred fast enough to/from reaction zone. In this case the polarization can
appear on both fuel and oxygen electrodes. When polarization is related to the steam conversion the limiting layer is fuel electrode. Overall concentration polarization depends on diffusivity of the components and their concentration, but also on porosity and structure of the electrodes and current density.

2.3.4 Advantages of solid oxide cells

Apart of the better kinetics due to the elevated temperature one of the reasons that solid oxide cells can reach such high electrical efficiencies is because significant part of the total energy supplied can be provided in a form of heat instead of more expensive electricity (**Figure 9**). Additionally, in the case of real electrolyzers the effect of ohmic heating due to the high current flow which is supplied to the electrodes should be taken into account. When the amount of Joule heat generated by the flow of electrons covers the reaction heat demand this is related to the so called operation at thermoneutral point. For high temperature electrolyzers this is a typical point of operation. The heat demand for electrolysis reaction is in this case covered by internal heat generation due to the irreversibility and losses. This allows operation with optimal flow of cooling air and high current densities above 1.3 A/cm².



Figure 11. The operating voltages and current densities for different types of electrolyzers [51] In case of low temperature electrolyzers (PEM, ALK, AME) the operating point is usually above the thermoneutral voltage. This is due to the fact that low temperature electrolyzers at thermoneutral voltage obtain low current densities and therefore small hydrogen generation. In existing PEM-based systems the electrolyzers operates at higher currents in order for higher

hydrogen production but this results in significant amount of heat generation on the electrolysis cells and external cooling has to be arranged decreasing in this way the system efficiency.

Moreover, SOC are characterized by a much lower operating voltage what means that the operational cost will be significantly lower because less electricity is needed for production of the same amount of hydrogen. Besides that solid oxide electrolyzers can be operated at quite high current densities in comparison to other types of electrolyzers especially the alkaline type. This means that the amount of hydrogen produced from the active surface area is higher and in final system lower amount of cells will be needed to obtain similar production possibilities.

The thermodynamics of electrolysis, but also economic factors, support and drive further development of SOC-based electrolyzers. The technology is still at early commercialization stage and there is a need for many research and developments to be completed especially at scale up aspects and degradation issues.

2.4 Materials and SOC development

2.4.1 Geometrical design

In general the SOC is composed of three different layers two electrodes separated by the electrolyte. The layers arrangement can be executed in two basic geometrical designs: planar and tubular (**Figure 12**). In case of the tubular geometry the gas flows can be arranged to flow through the cell tube or when one of the ends of the cell is closed gas is delivered and collected at the same side.



Figure 12. Tubular (left) and planar (right) design of the SOC cell

In principle the electrodes and electrolyte can be very thin to decrease the resistivity of each layer. However to provide the proper mechanical stability of the cell the basic three functional

layers needs to be supported to prevent mechanical failure. The most common approach is to make one of the layers thicker in which case the layer itself become a cell support. Therefore we can distinguish three types of SOCs:

- Anode Supported Cell, ASC,
- Cathode Supported Cell, CSC,
- Electrolyte Supported Cell, ESC.

Additionally, if the support is provided by a different material than three functional layers there are two more new designs that can be identified:

- Metal Supported Cell (MSC),
- Inert Supported Cell (ISC).

In MSC design the metal support serves as electron conductor, but do not contribute to the electrochemical processes taking place in the cell. In ISC design the support material is electrochemically and electrically neutral and electric connection has to be arranged by other means. **Figure 13** shows five different geometric configurations that can be found in planar solid oxide cells. The thicknesses of the layers in **Figure 13** are not in scale, but typically the electrolyte thickness is $3-20 \ \mu\text{m}$, fuel electrode $5-15 \ \mu\text{m}$, air electrode $15-80 \ \mu\text{m}$. The supporting layers usually have up to $1,000 \ \mu\text{m}$.



Figure 13. Various types of geometric configurations of solid oxide cells (layers depiction in electrolysis mode)

Cells produced on electrolyte support usually operates at higher temperatures then others types (>800 $^{\circ}$ C) due to high ohmic ionic resistance of thick electrolyte layer. Most commonly used anode supported cells has an operating temperature of 650-700 $^{\circ}$ C.

2.4.2 Materials used in SOC

The typical materials used in SOEC are basically similar to those used for SOFC [52]. The **Figure 14** presents the list of grouped materials most commonly used for various layers in SOC cells.



Figure 14. Most commonly used materials in SOC technology

2.4.2.1 Electrolytes

The electrolyte is the most crucial component in electrochemical cell. Its main roles are: (1) to ensure physical separation between anode and cathode gas compartments to prevent gas leakage, and (2) transport of oxide ions between cathode and anode. Additionally, good electrolyte needs to be chemically resistant to both oxidizing and reducing conditions which occurs on each side of the cell. In solid oxide cells most commonly used are ceramic metal oxides. The fluorite-type crystal structure MO₂ that occur in zirconia, ceria and bismuth oxide is one of the most commonly used today. In crystalline lattice oxygen vacancies can be introduced by substitutional doping like substitution of Zr^{+4} ions in ZrO_2 by Y^{+3} ions (Figure 15) [53].



Figure 15. Cubic structure and vacancy creation in YSZ by substitutional doping of ZrO₂ by Y₂O₃ [53]

Oxide ion transport is ensured by vacancy migration mechanism. The fluorite crystalline structure of this materials has oxygen vacancies where oxygen ion can be transported via "hoping" which can be described as an thermally activated process with specific activation energy of vacancy migration.

The ionic conductivity depends on the vacancy concentration and vacancy mobility

$$\sigma_{ion} = [V_o^{"}] \times 2e \times \mu_V \tag{Eq. 35}$$

 $[V_o^{"}]$ - concentration of oxygen vacancies in the lattice

- mobility of the oxygen vacancies that can be expressed by:

$$\mu_V = \frac{\mu_o}{T} \exp\left(\frac{-E_A}{kT}\right) \tag{Eq. 36}$$

 μ_0 - preexponential factor of the vacancy mobility

 E_A - effective activation energy of vacancy migration

Therefore the oxide ion conduction can be expressed as:

$$\sigma_{ion} = [V_o^{"}] \times 2e \times \frac{\mu_o}{T} \exp\left(\frac{-E_A}{kT}\right)$$
(Eq. 37)

The electrolyte electrical resistance at the time of cell operation which is one of the main factors for performance evaluation can be expressed by:

$$R_e = \frac{d}{A} \times \frac{1}{\sigma_{ion}} \tag{Eq. 38}$$

 R_e is dependent on oxide ion conductivity and geometry of the electrolyte material. The electrolyte resistance is decreased with lowering thickness (d) of the material or with surface

area (A) enlargement. This equation also shows that the higher the conductivity the lower resistance. Even though the conductivity depends on the chosen material the best electrolyte is not always the one with the highest conductivity. Currently most know and state-of-the-art electrolyte material is dopped zirconia. Zirconia based electrolytes do not have exceptional conductivity but its advantages lay in chemical stability and durability in the reducing hydrogen atmosphere, ease and low cost of manufacturing. Additionally, zirconia oxide is chemically neutral with NiO which allows production of Ni-YSZ cermet fuel electrode (the state-of the art electrode). However, doped zirconia during sintering with some of the electrode materials containing Sr may form an insulating layer of SrZrO₃ between the electrolyte and electrode [54]. Common practice to prevent formation of this phase is to introduce and interlayer of doped ceria [55]. Due its remarkable stability yttria stabilized zirconia remains still the most widely implemented in application electrolyte material to date.

In [56], research was carried out concerning an electrolyte Zirconia stabilized with Sc. The work showed that 10Sc1CeSZ is a promising material for both fuel cell and electrolysis applications, with good stability. To analyse the electrolyte material the test were carried out with platinum electrodes. They managed to achieve high current densities at a temperature of 700 °C. As part of the research single cell Ni-YSZ / 10Sc1CeSZ / Pt were also tested in 900 °C, in the electrolysis mode cells achieved current densities of -0.45 A/cm² at 1.5 V while ASR value reached 0.99 Ω cm².

A further promising electrolytes especially for intermediate temperatures are ones based on ceria. Similarly to the zirconia ceria has to be doped to obtain high oxygen vacancies concentration. In this case the most common dopants are Gd⁺³ and Sm⁺³ ions. Gadolinium doped ceria (GDC) and Samaria-doped ceria (SDC) characterize low activation energy and good conductivity, but in electrolysis mode may suffer some partial reduction phenomena [57].

2.4.2.2 SOC electrodes

The solid oxide cell electrodes are crucial for good cell performance and stable operation. The most vital attribute is that the electrode material has to exhibit high electrocatalytic activity, ionic and electric conductivity in the operating temperature. Additionally it has to be chemically stable and be compatible with electrolyte material in terms of chemical reactivity and comparable thermal expansion. On top of that the electrodes for SOC need to be mechanically

stable since they have to be sufficiently porous to ensure desired gas transport. The task of each electrode is different and will be described in this section.

2.4.2.2.1 Fuel electrode

The fuel electrode is responsible for extraction of oxygen ions from water molecules in order to obtain hydrogen production. In water steam electrolysis mode the overall fuel electrode reaction is:

$$H_2 O_q + [V_o^{"}] + 2e^- \leftrightarrow H_{2,q} + O_o^{2-}$$
 (Eq. 39)

 O_o^{2-} - oxygen ion on oxygen site in the electrolyte crystalline lattice

 $[V_o^n]$ - vacancy in oxygen site in the electrolyte crystalline lattice

The reaction takes place when electrons in the electrode, the gas phase and oxygen vacancy in the electrolyte are met at the so-called triple-phase boundary (TPB), only then the conversion of the electrical energy into chemical energy takes place. The most common fuel electrode material used for solid oxide cells is Ni-YSZ cermet (**Figure 16**).





It is a composite of NiO and YSZ invented by Spacil in 1970 [59]. The idea was to combine Ni which is a very good catalyst but has a big mismatch of thermal expansion coefficient (TEC)

with a electrolyte material and create porous composite that is good electric conductor and extends gas transport across the fuel electrode. YSZ stabilize the structure of Ni and makes Ni-YSZ composite quite stable, but also develop active sites and creates more TPB area across the fuel electrode volume. The high difference of TEC between YSZ (11×10^{-6} K⁻¹) and Ni (14×10^{-6} K⁻¹) is also mitigated in composite by carefully chosen ratio of the materials (**Figure 17**) [60].



Figure 17. Dependence of the thermal expansion coefficient (TEC) on NiO content in YSZ electrolyte [60]

The porosity of Ni-YSZ fuel electrode is also optimized to maintain the material structure and allow proper transport of gaseous reactants and products in the electrode [61]. The common approach is to prepare the fuel electrode as a multilayered structure in which different requirements can be satisfied. To organize that, the particle size gradient is introduce across the electrode. Different interlayers have also different Ni/YSZ ratio and porosity that changes with electrode depth. In the typical fuel electrode three functional layer can be distinguished. The first layer from the electrolyte side is the most active layer. Its main purpose is to drive the electrochemical reaction that is why it is characterized by fine Ni and YSZ particles size in order to extend the reactive TPB and reduce the polarization resistance. In order to prevent electrode/electrolyte delamination the TEC should has a close match.

The middle layer is present only in the fuel electrode supported cells. High porosity with a middle size grains characterize this layer. The top layer is so called contact layer which is responsible for a good connection to the interconnects. It usually is very porous to not limit the gas transfer and constructed with bigger grain size Ni particles in order to sustain good electrical conductivity (**Figure 18**).



Figure 18. Picture of the fuel electrode microstructure and components composition change across the electrode thickness [60]

There are recommendations to use dedicated materials for alternative modes of electrolysis operation. For example for co-electrolysis some spinel-based oxides were studied as potentially attractive materials for cathodes [62], for possible utilization of flue gases and the recovered steam, redox-stable LSCM perovskite material: La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} is proposed [63] and other (nano-particles of GDC, thiospinels or metal sulfides for higher tolerance to contaminants, LSCM electrolysis without hydrogen).

2.4.2.2.1 Oxygen electrode

The oxygen electrode is responsible for the oxygen exchange between electrode material and gas phase. Therefore it has to show good stability in highly oxidizing environment that is present in oxygen electrode compartment. In order to enhance cell performance it has to exhibit high electronic and ionic conductivity. Futhermore, a good catalytic activity and chemical stability in contact with electrolyte is expected from the fuel electrode materials. During operation in electrolysis mode the oxygen ions migrating from the electrolyte has to be conducted and released from the electrode. The overall oxygen electrode reaction is:

$$2O_o^{2-} \leftrightarrow [V_o^{-}] + 4e^- + O_{2,q}$$
 (Eq. 40)

Because the reaction is taking place at the oxygen electrode has a slower kinetics then one occurring on the fuel electrode, the polarization of the cell is highly dependent on the performance of the oxygen electrode. due to that during the last decades the work on the development of materials and structure for the oxygen electrode has been substantial. Currently the most commonly used materials for oxygen electrodes are ceramic oxides from the groups of perovskites and its derivaties. In this groups we can find electron conductors, oxygen ion

conductors or materials that exhibit both conductivities MIEC (Mixed Ionic Electric Conductors). In case of electronic conductors the oxidation/reduction of oxygen occurs close to the TPB. To extend the active area the common approach is to add electrolyte material to the electrode material and build porous two components electrode. One of the most important oxygen electrode materials is strontium-doped lanthanum manganite (LSM). It is widely used for SOC production and especially in the fuel cell mode remains the basic oxygen electrode material choice for temperatures 800-950 °C. LSM is purely electronic conductor and in order to extend the TPB range it is usually mixed with electrolyte material [64,65] (Figure 19 a, b). Example of this solution is one of the most common composite LSM-YSZ electrode.

In case of MIEC there is no need to use composites since ionic and electronic conductivity is already provided by one material. Since ions and electrons can travel across the bulk of the material the exchange area is substantially increased and the electrochemically active area is increased from TPB spots to the broader surface area of the porous electrode (Figure 19c) thus enhancing the electrode performance [66]. One of the most interesting and widely accepted MIEC materials are Lanthanum Strontium Cobaltite (LSC) and Lanthanum Strontium Cobaltite Ferrite (LSCF) [52]. Both of this materials have excellent catalytic properties and high electronic and ionic conductivities what makes them perfect candidates for electrodes. However Co-containing perovskites easily reacts with YSZ electrolyte. Because of that thin layer of other electrolyte material (typically GDC) is usually introduced to act as a barrier layer and prevents this interaction [67]



Figure 19. Different approach to the oxygen electrode design in SOC. a) porous single phase electronic conductor, b) porous composite of ionic and electronic conductor materials, c) porous mixed ionic electric conducting phase.

2.5 Experimental methods for analysis of solid oxide cells

The characterization of the quality and performance of the cell can be divided into two major characterization techniques: electrochemical analysis and structural components analysis. Electrochemical characterization includes methods such as: I-V measurements, EIS, long-term voltage monitoring, while the structural analysis incorporates various microscopy and diffraction methods to investigate the morphology, grain size, microstructure, layers composition, and interphase stability of the cell compartments.

2.5.1 Current-voltage measurements (I-V)

This technique is the most commonly used method for the evaluation of performance of electrochemical cells and stacks. The results of current-voltage analysis are often represented by so-called I-V curves (

Figure 20) since it is a measurements of cell voltage as a response for many individual current steps (galvanostatic operation). The result of this analysis is quantitative performance of the cell (to allow direct comparison of different size and shapes of the cells it is common to present results on I-V curves where I is current [A]). The shape of the I-V curve also may indicate the main loss contributions (such as activation, ohmic, concentration losses). Current-voltage analysis has to be performed in carefully chosen conditions that are stable during measurements.



Figure 20. Representation of I-V curve for electrolysis and fuel cell operation

One of the most important parameters that has to remain stable during I-V measurements is temperature. Current load and current supply is heavily influencing the temperature of the cell. In the fuel cell operation the heat is generated on the cell as a result of the ongoing reaction. This extra heat may change the operating temperature. In the electrolysis mode the situation is more complicated since at lower voltages the heat has to be supplied to the electrolysis reaction but over the thermoneutral voltage the heat is also generated due to the passing current. The rate of current change during the measurement is essential to keep the stable conditions. The current step can be realized at slow pace and the temperature control (e.g. furnace/heaters temperature setpoint) has to be adapted to the changing conditions. On the other hand, the current steps could be taken at higher rates to limit the overall measurement time, in order to end measurement before the temperature change will influence the voltage readings.

Another important parameter that has to be chosen carefully is reagents flow rates that are supplied from mass flow controllers to anode and cathode compartments. One of the way to realize proper I-V measurement is to kept the constant flow rates during the entire measurement. The flows has to correspond to the planned current densities in order to ensure reactants utilization below planned level. At higher flows the performance of the cell is usually improved because the reactant utilization is lower and the conditions across the cell itself are more evenly distributed.

Different approach to the flow of reagents may be to keep the reagents utilization levels at constant level during the measurement. This has to be realized by adjusting the flows at each current step. This approach however is more technically complicated (it needs very high precision and dedicated range of mass flow controller) and constant flow method is more commonly used.

2.5.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an alternating current technique that first concept was proposed by Oliver Heaviside in 1880s [68]. The method was developed and adapted in 1920s to be extensively used in semiconductors and ionic systems [69]. From that on it became a very useful tool across many fields including corrosion processes, monitoring of the coating properties and electrochemical cells [70]. During the EIS measurement the cell is subjected to a sinusoidal current or voltage signal applied at different frequencies. Normally the excitation signals are of quite low amplitudes [71]. The system response is then measured and analyzed to obtain information about various processes and loses in the cell as a function

of frequency. This method is used to distinguish the influence of different main sources of loos in the cell (ohmic, activation, concentration). This is one of the best known techniques for electrochemical cells analysis, but quite sophisticated equipment (**Figure 21**) is needed to perform measurements [72].



Figure 21. Example of impedance spectrometer used for electrochemical characterization (Zahner Zennium spectrometer with a 4-quadrant potentiostat, IPE-NRI).

The EIS measurements can be performed in potentiostatic or galvanostatic mode. During the measurements in potentiostatic mode voltage signal is applied while the current response is obtained. This approach is usually adapted for systems with high impedances in order to avoid high currents flows. On the other hand the galvanostatic mode is often used during measurements of small impedances since in this mode the current change is forced and voltage response is measured.

The Impedance is described by letter Z and it is a ratio of time dependent voltage and current

$$Z = \frac{V(t)}{i(t)}$$
(Eq. 25)

If we are applying a sinusoidal signal voltage at time t can be represented as:

$$V(t) = V_0 \cos(\omega t) \tag{Eq. 26}$$

Where V_0 is the voltage signal amplitude, ω is the radial frequency. Additionally the current response that was excited in the system can be described as follows:

$$i(t) = i_0 \cos(\omega t) \tag{Eq. 27}$$

Where i_0 is the current response amplitude



Figure 22. A graph of the relationship between a sinusoidal voltage signal that results in phaseshifted (ϕ) current response [72]

The current response obtained from the electrochemical system may be shifted in phase in comparison to the voltage sinusoidal signal. The phase shift is often described by letter Φ .

When we introduce the phase shift to the impedance equation we can write:

$$Z = \frac{V_0 \cos(\omega t)}{i_0 \cos(\omega t - \phi)}$$
(Eq. 28)

Substituting $Z_0 = \frac{V_0}{i_0}$ we can write impedance equation:

$$Z = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$
(Eq. 29)

The equation can be also represented in complex notation where $j = \sqrt{-1}$:

$$Z = \frac{V_0 e^{j\omega t}}{i_0 e^{j\omega t - j\phi}}$$
(Eq. 30)

Finally the system impedance can be expressed in terms of two components: impedance magnitude Z_0 and phase shift ϕ :

$$Z = Z_0 e^{j\phi} \tag{Eq. 31}$$

Or alternatively in terms of real and imaginary component:

$$Z_{real} = Z_0 \cos \phi \tag{Eq. 32}$$

$$Z_{imag} = Z_0 \sin j\phi \tag{Eq. 33}$$

$$Z = Z_0(\cos\phi + j\sin\phi)$$
 (Eq. 34)

The most common graphical representation of the impedance data is Nyquist plot where imaginary and real components are plotted together Z_{real} on x-axis and $-Z_{imag}$ on y-axis. The Nyquist graph usually shows the system impedance across vide range of frequencies (from hundreds of kHz to fractions of mHz) and has to be measured in linear part of the I-V curve or at very small amplitudes (e.g. 10 mV). The theoretical Nyquist plot obtained for the electrochemical cell is showed at **Figure 23**.





We can see that the plot shows two semicircular arcs. The size and shape of the individual semicircles represent the actual physics processes and material characteristics of a real cell and can be attributed to electrochemical losses of the electrodes. Additionally, the intersections of

the x axis and semicircles marks the values of three characteristics impedances. The first intersect marked as Z_{Ω} represents the ohmic impedance which is directly related to the ohmic losses in the electrochemical cell.

The example of use of impedance spectroscopy was shown by [73]. The comparison of two types of SOEC, metal supported (MS-SOC) and anode supported ASC cells was investigated during operation in the electrolysis mode. The impedance measurements and the voltage change during stable 120 h operation reveled degradation rate of MS-SOC was 3 times higher than ASC. The comparison of impedance spectra is presented in **Figure 24**. The impedance measurements help to analyze the degradation of both cells and shown specific behavior of the metal supported cell which ohmic resistance was decrease with rising current densities.



Figure 24. Comparison of the impedance spectra of anode supported cells ASC and metalsupported cells MSC before (left) and after (right) 120 h electrolysis operation [73]

2.5.3 Scanning Electron Microscopy (SEM) and EDS analysis

The electrochemical measurements and voltage monitoring can detect the degradation processes occurring during cell operation. In co-operation with structural analysis this techniques are commonly used for degradation monitoring. One of the most useful techniques for detection of microstructural changes is scanning electron microscopy (SEM). SEM is dedicated for direct analysis of morphology of the main components of the cells. It's inherent advantages over optical microscopy is high resolution and high magnification. To obtain full spectrum over degradation mechanics the analysis is usually performed with the samples before and after the test. The photographs are obtained by direct operation of high energy focused

electron beam on the examined surface and analysis of the secondary and backscattered electron signals [74]. The principle of operation of electron microscope is presented in **Figure 25**.



Figure 25. Interactions between primary electron beam and the sample during Scanning electron microscopy measurements [74]

The primary electrons (PE) are focused in high energy beam (0.1-50 keV) and guided on the examined surface. The electrons from the beam then interact with the examined material surface and the secondary electrons (SE) are emitted and observed by SEM detector. Because SE have low energy (up to 50 eV) it is quite easy to deflect them and aim them to the detector which increase the quality of the signal. Additionally low energy electrons are easily stopped and cannot travel across long distances. Because of that the detector can recognize them only if they are emitted from the sample surface. This kind of measurement delivers vast amount of data about topographic contrast and makes this method perfect for high resolution surface analysis. The typical SEM picture is presented in **Figure 26**



Figure 26. SEM image of the SOC. Various layers of the cell can be visible by this technique [75]

Additionally the electron beam may cause the excitation of the outer shell electrons to emit characteristic X-ray signal that can be used in Energy Dispersive X-Ray (EDS, sometime referred as EDX) analysis. The energy of the emitted photons is unique for each element, therefore the analysis of the radiation can be used for identification of the chemical elements detected in the sample. Both qualitative and quantitative analysis can be performed by EDS technique what means than not only identification of the chemical element is possible bat also the composition and distribution within the sample. In essence, the gathered chemical data can be visualized in various ways. The EDS results combined with SEM pictures can be used for generation of the element distribution map or line scans. The example of the SEM/EDS analysis performed for SOC is presented in **Figure 27**.



Figure 27. EDS map of SOC fuel electrode cross-section [76]

2.5.4 X-ray diffraction (XRD)

Another technique that commonly used for analysis of the electrochemical cells is the X-ray diffraction (XRD). It is used for gathering quantitative structural information about the material, which includes crystal structure and orientation, but also chemical compound information. It is powerful technique for detection and analysis of crystal structure changes in electrochemical cells. With XRD measurements the chemical stability and phase changes of the electrode and

electrolyte materials can be monitored [77]. Additionally, the poisoning effects and formation of secondary phases can be observed what makes the XRD technique an important tool in analysis of electrochemical cells. For example, researchers found new crystalline phases in the LSCF oxygen electrode operated in electrolysis mode [78]. The changes were found to be independent of the current densities.



Figure 28. XRD results of the oxygen LSCF electrode, new peaks suggest formation of new crystalline phase [78]

2.5.5 Galvanostatic long-term voltage monitoring

The vital technique that is used for long-term analysis is galvanostatic operation and monitoring of any voltage changes during the measurements. During the galvanostatic operation the current applied to the cell is controlled by the operator. In dynamic operation current is changing in time and i-V curve can be obtained. In case when galvanostatic mode is set to constant value of the current and voltage of cell is measured it is called the galvanostatic voltage monitoring. This method can be used to observe the change of the cell voltage during long-term operation.

2.6 Degradation of solid oxide cells

The degradation of solid oxide electrolysis cells depends not only on the cell manufacturing processes, materials selection and its treatment, but also on the operating conditions that cell is subjected to, i.e. operating temperature, gas composition and quality, current density, load cycles, and many others. The degradation can be described as a loss of the cell/stack performance over the time. The performance drop in electrolysis mode can be detected as an increase of the cell's (or cells stack) voltage while its operation at constant current or as a

decrease in hydrogen production at constant voltage operation. The progressive degradation can be also detected and measured as a growth of ASR during the cell (stack) operation. The ASR can be calculated from the linear part of the I-V curves as described in 2.3.2. However, to detect the change in the ASR the comparison between initial value and actual value of ASR has to be carried out. If the change in ASR is found for the given operation time the degradation can be calculated and expressed in mV/1,000 h or %/1,000 h. This approach assumes the linear degradation, what is not always the case, and can only be measured periodically. In order to observe cell (stack) performance change during operational live common approach is to monitor the voltage evolution or the volumetric flow of hydrogen generated during electrolysis operation. The data concerning hydrogen production while operation can be gathered with a use of flow meters and gas analyzers, but in this case a dedicated often expensive equipment is needed. The most commonly and most practical is to monitor the voltage of the cell (stack) during the operation. The degradation of the electrolyzer cell or stack is related to the voltage increase under constant current conditions. The nature of this increase can have different character (Figure 29). The voltage can change linearly, in this case the degradation rate is more or less constant. If the voltage rise is progressive the degradation rate is time dependent. In some cases the voltage increase can have a sudden character where the voltage change rapidly over short period of time. However, in some cases, at the beginning of the cell (stack) live the negative degradation can be sometimes observed what can be related to the passivation of layers and microstructure rearrangement.



Figure 29. Different types of degradation behavior in the SOE cell or stack.

One of the good example of described degradation types is work done by [79]. The SOC cells manufactured at Risø National Laboratory have been tested in electrolysis mode. Their results show efficiency and durability obtained while operating in temperature range from 750 °C to 950 °C and current densities from -0.25 A/cm² to -0.50 A/cm². The results indicate that the cells have an initial level area specific resistance at the level of 0.27 Ω cm² in electrolysis at 850 °C. During long-term DC tests in electrolysis mode, the passivation effect was observed during the first 100 hours of electrolysis (**Figure 30**). Cells that have been passivated during electrolysis tests can be partially activated by running again in fuel cell mode or after several hundred hours of electrolysis in constant conditions.



Figure 30. Cell voltage as a function of time at constant electrolysis conditions. Pure O_2 at positive electrode and $pH_2O = 0.7$ atm and $pH_2 = 0.3$ atm. at negative electrode [79]

In work [80] they continued work on the degradation of cells in electrolysis. It turned out that changing the sealing on the side of the hydrogen electrode of the system showed that the previously observed passivation effect for the first several hundred hours of electrolysis tests it was the result of the glass seal used. After long-term measurements in the galvanostatic electrolysis mode at 850° C, load 0.5 A/cm², and a water vapor content of 50% in hydrogen the degradation was found to be mainly caused by the increasing polarization of the hydrogen electrode. The measurements showed a degradation of 2%/1,000 h. The voltage evolution of this test is presented in **Figure 31**. *Post mortem* analysis of the samples tested under these

conditions for over 1,300 h found that the electrode microstructure was stable at these conditions for over 1300 h, but the presence of impurities was found. However, tests conducted at high current density (-2 A/cm^2), high temperature (950 °C), and the partial pressure of steam at the level of 90% led to microstructural changes at the fuel electrode-electrolyte interface.



Figure 31. Voltage evolution for 3 different electrolysis test. Test A, B, - albite glass sealant was used, test C - gold foil and platinum paste sealing. [80]

There are many factors that lead to the degradation processes in solid oxide cells and stacks. Watton in his doctoral dissertation [81] performed experimental analysis concerning the degradation of SOC. He carried out measurements in alternating mode and operated the cells in both, SOFC and SOE modes. Results showed that at the low current densities, cells degrade much faster in the electrolysis mode comparing to the SOFC. Obtained results may also suggest that the observed degradation is partially reversible and that the degradation origins are different for SOFC and SOE.

The next parts of the dissertation will summarize the typical degradation processes identified for SOC operated in electrolysis mode that are attributed to each of the cell layers.

2.6.1 Fuel electrode degradation

Fuel electrode performance depends on many structural parameters of the material such as: porosity, active area, particle size, and its distribution and others. Crippling of this parameters may lead to reduction of electrical conductivity and limitation of TPB area. In case of the most commonly used fuel electrode material which is Ni/YSZ cermet there are few identified degradation processes and all influence the microstructure of the electrode by agglomeration, coarsening or oxidation of the Ni particles. Keane in work [82] investigated the degradation of

Ni-YSZ fuel electrodes (SOEC cathodes). The dependence of the materials used, preparation techniques and operating conditions was analysed. The mentioned work highlighted importance of the nickel grains size for optimal performance, which in his case he found out to be changing depending on operating conditions (**Figure 32**). Additionally, it identified that agglomeration reduced the nickel interconnection and contact with the current collector.



Figure 32. SEM cross-sectional microstructure of the Ni-YSZ electrodes; a) NiO-YSZ assintered; b) Ni-YSZ after NiO reduction; c) tested in 15% H₂, 3% H₂O at OCV; d) tested in 15% H₂, 3% H₂O at 0.5 V; e) tested in 11% H₂, 30% H₂O at 0.8 V; f) tested in 30% CO, 70% CO₂ at 0.5 V. [82]

2.6.1.1 Ni- coarsening

One of the fuel electrode degradation phenomena is Ni-coarsening. This effect is related the morphological changes in the cermet microstructure due to the Ni particle growth and agglomeration in bigger grains. The effect is related to the operating current [83], and may lead to significant decrease of the TPB surface and finally means higher cell resistance. The Nicoarsening was firstly found in samples operated in fuel cell mode [84, 85]. Simwonis [86] reported this occurring at temperatures above 800 °C with non-polarized samples, also confirmed by [87] where 3D study of SOC microstructure evolution was performed during annealing in dry hydrogen at 850 °C. Results showed that the coarsening effect lead to decreased connectivity in Ni particles network and also reduced the Ni surface area. In [88] the analysis of SOC operated in reversible mode shown that the coarsening occurs in both operating modes. A series of long-term tests in the fuel cell mode and electrolysis modes for Ni-YSZ // YSZ // LSCF-CGO cells were conducted. It was found that under similar operating conditions the degradation rate was higher in the case of electrolysis than in the case of the fuel cell operation. To clarify this issue, an investigation was carried out and advanced post mortem techniques as well as modeling were incorporated for the analysis. It was found that Ni coarsening during operation was not dependent on polarization, even though the agglomeration explained much of the cell degradation. The fuel electrode composition was also found to have a significant influence on nickel coarsening. The faster growth rates were found in case of nickel-rich electrodes [89]. However, the most of the research suggest that the initial period of 200 h is the most essential for Ni growth rate which stats to decrease afterwards. Also humid environment has an amplifying effect on Ni grains growth in the initial phase. In [90] an attempt was made to approach degradation mechanisms in SOC cells from analytical side. An analytical model of Ni agglomeration in the Ni/YSZ electrode fuel electrode was created, which allows for a quantitative description of nickel agglomeration. The model takes into account the structural parameters of the electrode, such as porosity and nickel content, as well as vapor content and flux flow rate. The idea to include in the model contact growth model and the Ostwald ripening gave good and reliable results.

However, the mentioned above factors that can influence the Ni grains growth the overall impact of Ni-coarsening phenomena on the cell performance depends very much on the quality of the cell microstructure. When microstructure of fuel electrode is developed and the TPB area and porosity guarantees good gas diffusion, the observed growth of the Ni grains will have negligible effect on the cell operating results. This is due to the fact that fuel electrode reactions

are not rate limiting for the process. Additionally the impact of the Ni-coarsening below 800 °C is also limited due to the slower kinetics of sintering and agglomeration processes. Nonetheless, while working with unoptimized cell microstructures and at high temperatures, it is necessary to monitor the fuel electrode for materialization of this phenomena.

2.6.1.2 Nickel depletion

While the growth of Ni particles is observable in SOC in both operating modes SOFC and SOEC the Ni depletion is characteristic for electrolysis only. It is also a kind of Ni relocation but this time the Ni particles are moved away from the electrode/electrolyte interface. This results in reduction of the density of TPB at the cathode/electrolyte interface and due to the lower Ni contents limits the electronic conductivity. In extremal depletion cases the final effect may look like the overall electrolyte thickness has increased. Many research has shown that the main factors that has a significant influence on the level of Ni depletion are current density [53, 91, 92, 93, 94], steam content [53], temperature and time [95]. The schematic view of the mechanism of Ni migration proposed by [93] is presented in **Figure 33**.





Researchers performed the long-term measurements of SOEC performance at high current densities (1.5-2 A/cm²) in co-electrolysis mode. They operated the cell at gas conversions: 45% at 1.5 A/cm² and 60% at 2 A/cm², the cell was operated for 700 hours. The detailed electrochemical analysis showed a significant increase in the ohmic resistance, the transport resistance of oxide ions in Ni-YSZ composite electrodes and the resistance of the electrochemical reaction at the three-phase Ni-YSZ boundaries. However, the decrease in

efficiency was mainly attributed to microstructural changes in the Ni-YSZ electrode near the YSZ electrolyte, including the loss of the percolative Ni, the loss of contact between the Ni and YSZ electrolyte, and the decomposition of the YSZ near the Ni-YSZ/YSZ interface. The assumed mechanism is that Ni is evaporating during operation in electrolysis mode and then diffuses in gaseous phase as nickel oxide NiO or nickel hydroxides Ni(OH)_x.

The described phenomena of nickel depletion is still one of the most urgent problems to solve within the technology. The degradation of SOC performance that it leads to raise some concerns about technology commercialization and hydrogen mass production via high temperature electrolysis.

2.6.1.3 Carbon deposition in co-SOEC

The carbon formation and its deposition on the porous fuel electrodes is a well know process and extensively researched [96, 97, 98]. It is usually found during SOFC operation where presence of various carbon containing fuels and good kinetic conditions may lead to soot deposition. The process and it rate was found to depend on many conditions such as: temperature, pressure, fuel, presence of the catalyst, Steam to Carbon Ratio (S/C) or even on gas velocities [99]. The carbon formation takes place via Boudouard reaction:

$$2CO \to C + CO_2 \tag{Eq. 41}$$

or when other carbon containing gases are present through hydrocarbons decomposition:

$$C_n H_m = nC + \frac{m}{2} H_2$$
 (Eq. 42)

In steam electrolysis the danger of carbon deposition disappears since there is no gas containing carbon in the system. However, when a co-electrolysis is considered the simultaneous steam and carbon dioxide electrolysis takes place and mixture of CO/CO_2 containing fuel is present in the fuel electrode environment. The article [100] examined the risk of carbon deposition on the Ni-YSZ electrode during the co-electrolysis. The analysis was done for five different samples operated in constant current conditions, the measured voltage degradation during the test is presented in **Figure 34**. The current densities has been kept high between 1.5 and 2.25 A/cm^2 , and the average steam and carbon dioxide utilization level was below 66.8%. After the test, in the case of two cells delamination and carbon nanofibers in the Ni-YSZ / YSZ interface has been found. The observed carbon formation may be caused by gas diffusion limitations at

high current densities. Carbon nanofibers were only observed near the YSZ electrolyte, what may indicate a large overpotential gradient in TPB near the electrolyte.



Figure 34. Cell voltage degradation of the SOECs during galvanostatic operation at the current density of 1.5 A/cm², 2.0 A/cm² and 2.25 A/cm²; 45% H₂O + 45% CO₂ + 10% H₂ was supplied to the Ni-YSZ electrode and O₂ was supplied to the LSM-YSZ electrode. [100]

2.6.2 Electrolyte degradation

The most commonly used electrolyte in SOC cells, YSZ is characterized by high ionic conductivity and excellent chemical stability in both oxidizing and reducing atmospheres. Its stability is however put into extreme while operating in highly corrosive electrolysis conditions and some degradation effect has been noted. In [101] the 9,000 h test was performed in electrolysis mode with SOC cell with YSZ electrolyte. The cell exhibited almost 4%/kh degradation during operation at current density -1 A/cm². The performance loss was attributed to the electrolyte degradation. The *post mortem* analysis revealed substantial changes in electrolyte layer (**Figure 35**). The microstructure showed longitudinal porosity and severe pore formation at the grain boundaries.



Figure 35. Microstructural analysis of YSZ electrolyte layer after 9,000 h operation in electrolysis mode. a) horizontal structured pores; b) fracture found on the YSZ grain surface [101]

In the paper [102] researchers investigated scandia and ceria stabilized YSZ (10Sc1CeSZ) as an electrolyte for electrolysis cells. The tests were carried out at 800°C for two electrolyte supported cells one operated at 1.8 V and second at 2.8 V. *Post mortem* analysis showed various changes in the 10Sc1CeSZ electrolyte for the sample operated at higher voltage. The change of the crystal structure from cubic to rhombohedral was found, appearing first in the vicinity of the Ni-YSZ electrode and then progressing along the electrolyte layer. The change in structure was confirmed in XRD studies (**Figure 36**).



Figure 36. XRD analysis results indicating the crystal structure change in 10Sc1CeSZ electrolyte sample operated at in electrolysis mode at 2.8 V (LSM01). C -cubic phase of the ScSZ; β - rhombohedral phase (Sc₂Zr₇O₁₇) [102].

2.6.3 Oxygen electrode degradation

During electrolysis operation of solid oxide cells the oxygen electrode degradation is one of the most important contributors to the degradation of the cell. The operation at high current density from the point of view of technology application is much more economically beneficial, but especially in these conditions the oxygen electrode starts to demonstrate higher degradation [103]. In order to improve the performance various degradation processes e.g. electrode delamination, chromium poisoning, secondary phase formation, need to be firstly addressed. Here some of the known operational problems with oxygen electrodes will be mentioned with a focus on three most widely used oxygen electrode materials (LSM, LSC, LSCF). Each of this materials is dedicated for operation in slightly different temperatures because of its intrinsic properties and ionic conductivity. LSM material is usually applied at higher operating temperatures (>800 °C). While LSC can be used in temperatures as low as 650 °C and LSCF for intermediate temperature electrolyzers (700-800 °C).

2.6.3.1 Electrode delamination

The delamination of the oxygen electrode from electrolyte or barrier layer is one of the limiting issue with wide application of LSM electrodes in electrolyzers systems leading to the decrease in time of production of hydrogen (**Figure 37**). The Idaho National Laboratory (INL) was engaged in research to solve technical and degradation problems related to SOEC. The work [104] provides a summary of the research that included stack testing, post-test study, degradation modeling aimed to identify and compare the degradation mechanisms in SOEC and SOFCs. One of the conclusions was that the oxygen side has a much greater impact on the observed degradation in electrolysis mode due to delamination of large areas of the electrodes. Based on the *post mortem* analysis the degradation of electrolysis stacks was largely controlled by the delamination rate of the LSM oxygen electrode. The electrode delamination is a severe problem that results in increased ohmic loses and reduction of reaction active area. The problems were found even at short term operation [105].



Figure 37. Area-specific resistance of a 25-cell stack as a function of time for a 1,000-hour test [104]

The LSM delamination issue has been attributed to be caused by various processes. In research analysis [106] in order to identify the degradation mechanism researchers used symmetrical cells consisting of yttrium oxide stabilized zirconia electrolyte (YSZ) and composite electrodes (LSM) / YSZ and a ring platinum reference electrode. LSM deactivation was identified to be resulting from the decrease in oxygen vacancies and changes in the surface of the LSM material under the high current operation.

Jacobsen in [107] suggested that during long-term operation in electrolysis mode the oxygen pressure can be built up in electrolyte cavities and in a results leads to the delamination. Also [82] in his work was analysing the delamination of lanthanum-manganite electrodes. He discovered that small lanthanum zirconate particles were formed at the anode side of the LSM-YSZ interface as a result of the high oxygen pressure build-up in the closed pores by oxygen ions recombination to oxygen. The resulting interfacial cracks and variability in thermal expansion weaken the LSM-YSZ interface, causing gradual delamination. Virkar has proposed an electrochemical model [108] to describe this phenomena concluding that addition of a small amount of a transition metal oxide or other oxides may decrease the tendency for delamination.



Figure 38. The illustration of the LSM/YSZ interface delamination mechanism. (a) oxygen migration between electrolyte and electrode grain, (b) local stress on LSM particles due to the LSM lattice shrinkage, (c) microcrack formation, (d) buildup of nanoparticles, (e) nanoparticles development (f) nanoparticle layers formation causing the delamination at the LSM/YSZ interface [105]

In the work [109] the degradation of the LSMC air electrode was investigated. Unlike the previous studies that found the causes of delamination in the disintegration of air electrodes, it was shown that delamination can also occur as a result of the barrier layer disintegration (in this case: samaria-doped ceria (SDC)). The formation of SDC nanoparticles was found and it is suspected that it weakens the contact between the air electrode and the barrier layer which can lead to electrode delamination.

After the exploration of delamination mechanism for LSM material the comparison of three different materials dedicated for the oxygen electrode was analysed in [110]. In their work, the authors conducted tests with various composite air electrodes: LSM, LSC and LSCF. The tests were carried out on full-scale 10 cm x 10 cm cells and compared in terms of performance and degradation in one stack consisting of three cells. During the tests, the stack was supplied with gases containing 90/10% (vol) H₂O /H₂. Initial characterization showed that the SOEC performance was in the following order: LSM, LSCF and LSC. The stack was then operated for 640 h in electrolyzer mode at a constant current density of 0.50 A/cm² at 750 °C. *Post mortem* analysis revealed that delamination occurred mainly in the steam and air inlet areas of the cells with LSM and LSC, with stronger delamination in the steam inlet area. No delamination was found at the cell with LSCF (**Figure 39**).



Figure 39. The cross section of the three different cells at the air inlet after electrolysis operation. Oxygen electrode delamination visible in the case of LSM and LSC. LSCF without delamination [110]

However, the delamination of LSCF material is not that obvious like in case of LSM and LSC materials the results of *post mortem* analysis performed by [88] after a series of long-term tests in the fuel cell mode and electrolysis modes, shown the formation of nanopores and Sr diffusion (Figure 40). The SrZrO₃ layer formation at the electrolyte/barrier layer was found to occur mainly during electrolysis operation and is very limited in fuel cell mode. The measures higher degradation rates in the electrolysis were associated with a higher LSCF de-mixing rate.



Figure 40. SEM images at the electrolyte/barrier layer of SOEC mode with the Sr-rich secondary phase, the Co-rich particles and line of nano-pores at grain boundaries in the electrolyte [88]

As can be seen the extensive research concerning the delamination of oxygen electrodes indicates that low ionic conductivity of air electrode and possible disintegration of air electrode into nanoparticles and undesired phase formation constitutes some of the fundamental reasons of delamination processes.

2.6.3.2 Chromia poisoning

Among many of the degradation effects that have been found to involve oxygen electrode the chromium interactions with electrode materials is repeatedly referred as a major degradation problem. Due to the progressing trend of decreasing of the operational temperature od SOC the window of opportunity for use of low cost metallic materials has been opened and the universal ceramic interconnects are being systematically replaced. The high electrical and thermal conductivity combined with developed and cheap processing methods led to the introduction of Cr based alloys and ferritic steels as a primary interconnects materials [111]. Chromium based materials are convenient since the chromia oxides formation rate and scale growth is moderate and it's electronic conductivity is acceptable [112]. However, the presence of Cr₂O₃ scale that grows under oxidizing and/or humid conditions may lead to evaporation of chromium gaseous species: chromium oxide (CrO₃) and chromium oxyhydroxite (Cr(OH)₂O₂) [113]. Some of the evaporated Cr compounds may chemically interact with adjacent materials especially at the oxygen electrode side since perovskite materials are prone to interact with chromia species. These interaction usually cause the loss of electrochemical activity and overall cell performance [114]. The influence of the Fe-Cr alloys on the stability of the LSM oxygen electrode during operation in electrolysis mode was analysed by [115]. Authors found that the presence of metallic interconnect accelerates the degradation and delamination of the LSM electrode operated at 800 °C. Similar conclusion were obtained for LSC material after detailed chemical and structural analysis [116] which showed that the chromium was present in the electrode and the undesired secondary phases containing Cr were discovered. To limit the chromium effects, more sensitive electrode materials are replaced by more resistant ones (e.g. LSM replaced by LSCF). Different approach to mitigate chromium evaporation effects is to apply dense protective coatings on the steel interconnects. These are usually spinels based on doped cobaltite (Mn, Co, Fe)₃O₄ applied by various methods like dip coating, screen printing, electrophoretic deposition (EPD), plasma spraying or others. Another path leading to reduction of the chromium evaporation problem was made possible by the development of the interconnect materials (e.g. Crofer 22) that tend to form more stable oxides (Cr-Mn spinels) then Cr₂O₃ limiting the amount of Cr vapour pressure [117].

2.6.3.3 Sulfur poisoning

Sulfur poisoning problem usually concerns the fuel electrodes during operation in fuel cell mode since the fuels may contain some traces of the sulfur compounds. Sulfur is then absorbed

on the active sites of nickel causing reduction of the electrode reaction rate. However the oxygen electrode may also be affected with sulfur exposition. In [118] a comparison of durability between SOFC and SOEC cells was investigated under varying air supply conditions. Oxygen electrode material was LSC with the gadolinium-doped ceria (CGO) barrier layer between YSZ electrolyte. A high degradation rate was found during SOEC operation with compressed air (4.8%/kh). Tests for the presence of sulfur in compressed air showed the sulfur content at the level of 0.74 ppb. The comparison of voltage cell degradation during SOE operation is presented in **Figure 41**.



Figure 41. Comparison of voltage evolution for 3x SOEC supplied with: 1- compressed air (0.74 ppb of Sulfur content), 2 - filtered compressed air (0.12 ppb of Sulfur), 3- and no air, for 5,000 h [118]

Based on the microstructural and spectrometric analysis, it was found that the S poisoning of the oxygen electrode was the main cause of the observed high degree of degradation. It is noteworthy that S penetration in electrolysis mode was detected on the oxygen electrode side mainly at the CGO/LSC interface. In case of SOFC mode the sulfur was distributed rather separately within the oxygen electrode. The authors suspect that the high oxygen partial pressure at the electrolyte / oxygen electrode interface accelerated S penetration. When compressed air was filtered with activated carbon during SOEC operation, the degradation rate dropped to 0.6%/kh in 3,000 hours. In addition, the work included accelerated measurements using air containing 0.2 ppm SO₂. These studies suggest that the effect of S poisoning at the

oxygen electrode side is much more significant during SOEC operation than during SOFC operation.

2.6.4 LSCF as one of the state-of-the-art an oxygen electrode and its stability in the humid environment

This chapter is focused on the stability and overall behaviour of LSCF oxygen electrode material which was chosen as a primary electrode material for the experimental measurements presented in this thesis. In comparison to the other established and thoroughly analysed oxygen electrode materials the LSCF shows rather good stability during electrolysis operation without the tendencies for rapid degradations (see previous chapter concerning degradation phenomena in oxygen electrodes). However, the replacement of air by steam in the anode electrode during electrolysis operation may compromise the behavior of anode, and therefore will be the main subject of the experimental campaign which is described in details later in this thesis. Consequently, the stable and well known material such as LSCF is recommended for the mentioned research. Some of the measurements report very stable behavior of LSCF during electrolysis operation. In the work [119] an analysis the was carried out with cell with direct assembly of the LSCF air electrode on the YSZ electrolyte. The cell Ni-YSZ/YSZ/LSCF showed a very stable operation, without delamination for 300 h at -0.5 A/cm² and 750 °C. Microstructural analysis showed that Sr segregation and migration to the electrolyte/electrode interface was suppressed while operated in SOEC mode. However, Sr migration and formation of SrZrO₃ near the electrode/electrolyte boundary is the most commonly reported degradation mechanism of LSCF electrode. Contradicting results to the [119] were presented in [120] paper, a series of long-term tests with SOC cells was carried out. The cells operated in both, fuel cell and electrolysis modes. The composition of the cells layers was Ni-YSZ/YSZ/LSCF-CGO. Studies have shown that the degradation is significantly higher for the cells operated in the electrolyzer mode. Post mortem performed after each test showed Sr diffusion and SrZrO3 formation at the YSZ/CGO interface mainly occurs during electrolysis operations, while the process is very limited in fuel cell mode. It was suggested that it is the loss of free oxygen sites due to electrolysis polarization that may cause the release of Sr from the structure, which in turn may explain the obtained experimental results. The microstructural changes in LSCF electrode were also reported in [91] by SEM and microanalytical techniques. After operation for 6,100 h and 9,000 h under various current densities -0.75 A/cm² and -1 A/cm². Post mortem analysis discovered formation of SrZrO3 at anode side in pores near the electrolyte.

In the work [121] an analysis was carried with focus on the delamination of air electrode while operating SOEC cell. The LSCF material was sintered directly on the YSZ electrolyte. The cell was operated for 24 hours under the conditions of high current density 1 A/cm² at 800 °C. An increase in ohmic and polarization resistance was noticed and *post mortem* analysis found delamination of the LSCF layer. The authors described a possible mechanism causing these effects. They discovered that the sintering of the LSCF layer causes the formation of a dense layer of SrZrO₃ on the LSCF-YSZ interface, which due to its low porosity, causes the build-up of oxygen pressure and delamination of the LSCF layer during the electrolysis operation. Further investigation presented in the [122] paper was carried out on the problems of LSCF delamination on the YSZ. Six various configuration of half cells with LSCF electrode were tested at the temperature of 800 °C. The formation of the SrZeO₃ layer at the interface was also confirmed. It was found that increasing the sintering temperature can lead to a reduction in the degradation rate of polarization resistance.

To limit the reaction LSCF and Zr and in consequence SrZrO₃ formation, the direct contact must be avoided and therefore diffusion barrier layer between electrolyte and oxygen electrode is commonly introduced. In the work [123] the researchers analysed the influence of the GDC interlayer on cell stability. 100 hours tests were conducted at 800 °C under current densities of -0.8 A/cm² in electrolysis mode. Studies shown that the presence of a GDC layer between YSZ and LSCF material significantly reduced the problem of LSCF delamination during operation in the electrolysis mode, and also reduced the ohmic and electrode polarization resistances. Good stability of LSCF with GDC layer was also confirmed in [124] article, in which two types of SOECs were compared during co-electrolysis operation. The first has LSM/YSZ oxygen electrode second LSCF/GGC oxygen electrode. The degradation measurements were carried out at a constant current density of 1.5 A/cm² at the 800 °C. During the tests, a much lower degradation rate was reported for LSCF/GDC. Possibility to prevent Sr diffusion from LSCF material by GDC barrier-layer deposited on YSZ electrolyte was investigated in [125]. It was found that the density of GDC layer is crucial for Sr accumulation. During electrolysis operation at 0.8 A/cm² for 100 h cell with spattered dense GDC layer exhibit lower voltage degradation rate than cell with thick porous screen printed GDC. Post mortem analysis (Figure 42) showed that Sr accumulated at the electrolyte-GDC interface. Authors concluded that the Sr diffusion can be prevented if GDC layer is dense and crack free.


Figure 42. EDS analysis of two samples after electrolysis operation. Cell with sputtered dense and crack free GDC (left) screen printed thick porous GDC (right)

The stability of the LSCF oxygen electrode was also found to be related to the current applied during the electrolysis operation. In the work [126] LSCF material was experimentally tested and measurements were conducted at 800°C 2,000 h in electrolysis mode. During electrolysis operation at current densities of -0.3 A/cm² there was no degradation observed, but after the increase of current density to -0.875 A/cm² a 1.5%/kh degradation rate was measured. Different degradation stage were noted in [127] during 4,400 h electrolysis test of Ni-YSZ/YSZ/LSCF-CGO cell (operated at -1 A/cm²). The most of the degradation was attributed to the fuel electrode but some morphological changes of the barrier layer and LSCF-CGO electrode were found at the places where current densities were highest which mean close to the steam inlet to the cell. The remaining part of the cell did not undergo any changes.

Another important issue is the stability of the oxygen electrode in the presence of steam. There are only a few publications concerning the use of steam as a sweep gas in the oxygen electrode of SOE. However, the literature focuses mainly on the performance not on the stability of the material [128]. The chemical stability of LSCF material in pellet form at medium and high pressure of water vapor was investigated [129]. The analysis led to the result that in tested conditions LSCF exhibits very good stability. However, there are no information concerning LSCF stability during electrolysis operation. In the [130] paper, the influence of the presence of water vapor on the degradation while operating in the fuel cell mode was investigated. The work demonstrated that LSCF cathode exhibits no degradation during operation at 750 °C at various humidification levels (**Figure 43**).



Figure 43. Voltage evolution and influence of the air humidification on degradation of cell with LSCF cathode material. Measured at 750 °C, 0.41 A/cm², 10% OU, 4% humidified H₂ as fuel and 10% FU [130]

Stability of LSCF material operated as an cathode in fuel cell mode with H₂O was also confirmed in the [131]. It was found that LSCF has a good performance and stability while working in $O_2/CO_2(2.83\%)/H_2O(2.64\%)$ atmosphere at elevated temperatures >680 °C while exhibit high degradation at lower temperatures due to the low oxygen activation and surface diffusion.

The comparison of influence of humidification of air on two cathode materials LSM and LSCF was presented in the [132]. Authors conducted 1,000 h test with various steam content in air stream at 800°C. It was discovered that the degradation accelerate at higher steam concentration while at typical ambient air humidity LSCF is stable. Authors concluded that it is caused by gradual decomposition of the LSCF. The stability is also strongly influenced by the temperature and is decreased with decreasing temperature.

3. Experimental setup

In this section the experimental setup and testing procedures which were used in the experimental studies presented in the dissertation are described. The experimental facility discussed in this chapter is part of the Department of High Temperature Processes at the Institute of Power Engineering – National Research Institute in Poland. The IPE-NRI possess an unique infrastructure for conduction of professional, experimental investigation of the macro-scaled SOFC and SOEC size of 5 cm x 5 cm and larger. The used for this research laboratory is certified and properly equipped to operate with flammable gases, including H₂, CO, CH₄, and mixtures.

3.1. Test bench

The electrochemical characteristic and long-term measurements (I-V curves and EIS measurements, detailly described in the previous part of the thesis) were conducted in the dedicated test bench (Figure 44).



Figure 44. Dedicated test bench for measurements of single 5 cm x 5 cm cells

The main component of the stand is an electric furnace. It is equipped with four 1.5 kW heaters mounted on sides of the insulated hot chamber. Four side heating system ensures the smaller temperature gradients inside the hot chamber. The temperature is controlled with PID controller

and the N type thermocouple installed inside. The hot chamber is used to ensure the necessary temperature in the cell housing with electrochemical cell inside. The test stand is equipped with set of three Bronkhorst El-Flow mass flow controllers dedicated for hydrogen, nitrogen and air which are used for very precise gas delivery to the cell. The required gas humidification level that is necessary for SOC measurements is achieved thanks to the use of a precise Cellkraft P-10 laboratory humidifier. The humidification is controlled by the temperature control in the device. Additionally, for test in which steam was delivered to both electrodes the aThmos precise steam generator was used to deliver steam to the oxygen compartment. The humidified gas and steam are delivered to the system through the heated lines to prevent steam condensation.



Figure 45. Scheme of dedicated test bench for 5 cm x 5 cm single cell testing

The setup allows also a precise control over the compression force applied to the test section for proper cell sealing. The pneumatic compression systems is controlled by Bronkhorst El-Press pressure controller which controls the pressure in a pneumatic actuator. For proper cell characterization the test stand is equipped with a temperature and voltage data acquisition system with a dedicated software for data monitoring.

The electrochemical measurements of the cells were performed with a use of the Zahner Zennium spectrometer with a 4-quadrant potentiostat that enables the measurements of EIS impedance spectra and current-voltage curves in the fuel cell and electrolyzer modes. For longterm measurements constant current conditions were obtained with spectrometer by Fuel Con.

3.2. Test section

To conduct planned experiments with SOE cells a new design of the test section was elaborated. In order to limit the chromium evaporation and its influence on the stability of oxygen electrode high chromium containing steel of bottom plate has been replaced with a new *in house* solution based on material with much lower chromium evaporation properties.

The test section is a dedicated housing for a cells of 5 cm x 5 cm that consist of two main parts: top closing plate and bottom closing plate. The cross-section of the test section is presented in **Figure 46**. Each plate have gas channels which function is proper gas distribution to the surfaces of both electrodes of the cell. The process gases are delivered through steel pipes welded on the inlet and the outlet side. Additionally, the top plate also acts as a direct current collector from the fuel electrode. For precise temperature monitoring there are two N type thermocouple installed in the closing plates. The hold for the thermocouples is placed right below the gas channels this allows temperature measurements very close to the center of the electrochemical cell.

To ensure proper sealing of the cell the system also incorporates glass seals. Its role is to prevent leakage and gas crossover between electrodes and gas leaks to the furnace chamber. During operation, the bottom plate is placed in the middle of the furnace on the ceramic base. Top plate is pressed from the top by a pneumatic actuator mounted on the bench.



Figure 46. Test section used in the test bench for 5 cm x 5 cm single cell testing

The test section during the assembly is held upside down to allow easier handling of each part. In the first step the Ni-mesh is placed on gas channels of the top plate and then the cell is attached to the top plate with a glass sealant. The gold current collector is used on the anode side and a sheet is added to prevent shortcuts and the whole test section is closed with the bottom plate. At this stage the test section is carefully turnover and placed inside the electric furnace on the ceramic base plate. The housing and cell inside is initially pressed in order to hold the setup in place during the heat up phase, but this also prevent any undesired shift of the assembled test section during the connection of the gas pipes and thermocouples installation.

3.3. Cells characteristics

The 5 cm x 5 cm cells have been selected for the experimental analysis. This is a semi-technical size with active area of 16 cm² which can represent properties of the industrial grade cells with active surface of 5-10 times higher. In this work the standard Ni/YSZ cermet has been selected for the fuel electrode. The fuel electrode is not a main subject of analysis but its behavior will have an impact on the measurements (electrochemical characterization, determination of the degradation rate performance due to the alternation of the microstructure, impedance spectra). For that reason it is justified to select material which is well established and has been characterized in various conditions. As an electrolyte an 8YSZ was chosen as one of the most commonly used material with high ionic conductivity and good stability in high temperatures. On the oxygen side the LSCF with thin GDC barrier layer was applied. Interlayer is incorporated to limit the reaction of oxygen electrode material and electrolyte. This cell configuration sets are reference configuration which serves as a benchmark and will aid in proper interpretation of the results. Two different cell types (Type A and Type B) were used in this thesis. Both types are fuel electrode supported, but the support thickness is different and manufactured via different production methods (Type A -tape casting, Type B – High pressure injection molding [133, 134]). There are also some minor differences for electrolyte and GDC layer. However the oxygen electrode for both types of configuration are exactly the same and applied by the same technique at IPE-NRI. The comparison of the cell configuration for two types are presented in Figure 47 and Table 3.



Figure 47. Cell configuration and layers characteristics for two cell types use in the experimental campaign

Layer	ТҮРЕ А		ТҮРЕ В		
	Material	Thickness	Material	Thickness	
Oxygen electrode (OE)	$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$	30 µm	$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$	30 µm	
Barrier layer (BL)	$Gd_{0.1}Ce_{0.9}O_2$	3 µm	$Gd_{0.1}Ce_{0.9}O_2$	3 µm	
Electrolyte (E)	8YSZ	3-6 µm	8YSZ	4 µm	
Fuel electrode functional layer (FL)	NiO/8YSZ	10 µm	NiO/8YSZ 50/50 wt.%	7 µm	
Fuel electrode support (FS)	NiO/8YSZ	300 µm	NiO/8YSZ 66/34 wt.%	1,000 µm	
Fuel electrode contact layer (CL)	NiO	3 µm	NiO	3 µm	

Table 3. Basic specification of the cells used



Figure 48. SEM image of the reference type B cell cross-section

3.4. Procedures for conditioning cells

Before the electrochemical measurements each of the tested cells was conditioned in order to obtain proper sealing and performance - according to the test procedure developed over the years and used in experimental activities at IPE-NRI.

The heat-up and sealing procedure starts after cell installation in the test section and placement of the housing in the electric furnace. The procedure begins with the setting the flow of the process gases. The fuel electrode is swept by 100 Nml/min of 5% mixture hydrogen in nitrogen. To the oxygen electrode side 400 Nml/min of compressed dry air is delivered at all times during the initial procedures. When the gases are supplied to the test section the setup is heated up to the 850 °C at the rate of 60 °C/min. This is a softening temperature of the glass used for sealing. At this stage glass is being conditioned for 30 minutes, and in the next step the compression force is increased to 250 N. After this phase, the temperature is reduced to the 800 °C (cooling rate 60 °C/min) which is operating temperature of the cell chosen for this investigation. When the temperature is stable the cell needs to be subjected to the reduction process during which the NiO in fuel electrode is reduced to Ni. Part of the reduction took place during the heating up period in small concentration of hydrogen. In the next step the hydrogen content in the fuel mixture is gradually increased from 5 vol.% up to 50 vol.%. During this change the temperatures in housing are carefully monitored in order to detect major leakages that might manifest itself in significant temperature increase. If no leakage is found the cell is kept in this conditions for 3 hours for general reduction and further for 20 hours under low current load (0.1 A/cm²). As a confirmation of proper cell operation, after 20 hours the voltage loaded with 0.1 A/cm² should be higher than 1 V. Finally the cell is unloaded to measure the stable value of voltage under OCV conditions. This is also one of the parameter that indicates the integrity of the cell and potential leakages. If OCV is higher than 1.2 V the cell is classified as a ready for electrochemical testing.

3.5. Experimental techniques dedicated to degradation

After the heat up and conditioning procedures were finished the main electrochemical tests might begin. The investigation was conducted at 800 °C. The first step was to measure the starting performance of the cell and measure the influence of the presence of high content of steam on both electrodes. During this test the cathode composition was kept constant and the hydrogen gas was humidified to 70% (vol) with a use of Cellkraft P-10 Humidifier. The anode

gas composition varied in the initial test according to the table. During long-term degradation measurement the anode side was swept by pure steam delivered from the precise steam generator with rate of 500 Nml/min. The current load was set to -0.25 A/cm² what corresponds to ca. 14% of Steam Utilization on the cathode side. The EIS measurement was performed under the same current conditions approximately every 50 h. The set up used during the impedance spectra measurements is depicted in **Figure 49**.



Figure 49. Impedance spectroscopy set-up used for measurements of SOC operated in electrolysis mode

After 1,000 h of degradation measurements the conditions measured during the initial test was measured again in order to compare the performance at the beginning and after long-term test.

3.6. *Post mortem* analysis of cells

After high temperature electrochemical analysis the sample cell was cooled down and prepared for further material analysis. *Post mortem* analysis focus on search for any morphological changes and physical defects. To evaluate the microstructure of the functional layers and the contact between them after long-term testing in the electrolysis mode the SEM measurements extended by the EDS analysis were performed. The test were conducted using the Versa 3D (FEI) high-resolution scanning electron microscope equipped with EDX detector (Carl Zeiss AG, Oberkochen, Germany). The cross-section samples of the tested cells were prepared using Hitachi IM4000Plus ion polisher (Hitachi High-Tech Corp., Ibaraki, Japan), to eliminate surface irregularities and prevent cracks, delamination and rupture of the porous ceramic layers of SOC from sample preparation for SEM analysis. X-ray diffraction analysis were performed on CuK α radiation in 2 Θ range of 10-110° with step 0.013° using Panalytical Empyrean diffractometer with PIXcell3D detector.

4. Experimental results

To understand the behaviour of the investigated cells in proposed, novel operating conditions it is important to measure and investigate the initial state and parameters and understand the structural morphology of the cells.

In this chapter the experimental investigation will be presented. The experimental results part covers the electrochemical performance of the cell in various conditions, long-term degradation test and *post mortem* microstructural analysis.

4.1. Operation of the SOC cell under electrolysis mode with a steam as a sweep gas

4.1.1. Objectives

The objective is to obtain data concerning the degradation effect of the solid oxide cells related to the extreme humidity at the oxygen electrode side. Both, short and long-term electrochemical measurements and *post-mortem* microstructural analysis, carried out after long term operation, were performed.

4.1.2. Cell performance during long-term operation with steam as a sweep gas

The long-term performance of the solid oxide cells was measured in order to obtain the necessary data to estimate the degradation rate of the cell and degradation mechanism of oxygen electrode that was operating outside of the standard conditions. Five independent long-term measurements were conducted for different cells with a following general configuration Ni-8YSZ/8YSZ/GDC/LSCF.

The cells were operated in electrolysis mode with cathode gas composition of 70 vol.% steam and 30 vol.% hydrogen (CFG - Cathode Fed Gas). The total cathodic gas flow was kept in the range corresponding to the low steam utilization values. The oxygen electrode was supplied with pure steam during each run. In order to avoid the common degradation phenomena associated with the high current densities (see chapter 2.6 Degradation of solid oxide cells), mild current operation was chosen \leq -0.25 A/cm². This value corresponds to current equal -4 A as the active area of cells is 16 cm².

Tost	Duration	Cell	Current	Ano	de	Cathode	
number	[h]		[A]	Flow [Nml/min]	Comp. Vol.%	Flow [Nml/min]	Comp. Vol.%
Cell_1	>200 h	Type A	-2A	500 H ₂ O	100 H ₂ O	$120 \ H_2 + 280 \ H_2O$	70 H ₂ O
Cell 2	1,000 h	Type A	-4A	$500 \text{ H}_2\text{O}$	$100 \text{ H}_2\text{O}$	$120 \ H_2 + 280 \ H_2O$	$70 \ H_2O$
Cell 3	>600 h	Type B	-4A	500 H ₂ O	100 H ₂ O	$150 \; {\rm H_2} + 350 \; {\rm H_2O}$	70 H ₂ O
Cell 4	>300 h	Type B	-4A	500 H ₂ O	100 H ₂ O	$150 \; {\rm H_2} + 350 \; {\rm H_2O}$	70 H ₂ O
Cell 5	1,000 h	Type B	-4A	500 H ₂ O	$100 \text{ H}_2\text{O}$	$90 \; H_2 + 210 \; H_2 O$	$70 \ H_2O$

Table 4. Index of long-term measurements of SOEC operated with steam as a sweep gas

After preliminary calibration test the cells were stabilized at the nominal current load in the standard sweep gas conditions (air). When the voltage and temperature reached stable point, the steam was introduced to the anode side (air flow was gradually turned down). The cells were kept under these conditions and each cell voltage evolution during the long-term operation was recorded and is presented in **Figure 50**.



Figure 50. Voltage evolution during long-term measurements; Current density -0.25 A/cm². Flow composition C: 70 vol. % H₂O / 30 vol. % H₂; A: 100 vol. % H₂O

For every cell operated with steam as a sweep gas a noticeable voltage increase was found. After steam delivery to the cathode side the cell voltage was not stable and was constantly rising. In case of the Cell 5 starting voltage point was at 915 mV, but after 20 h of operation voltage increased to 1,014 mV (99 mV increase) which can be interpretated as a performance

drop by almost 11%. For this initial time the degradation rate was found to be around 5 V/kh, (540%/kh). The rate of voltage change was not constant, and it was slowing down. Between 20 h and 100 h of the measurement the value of operating voltage risen to 1,094 mV (additional 90 mV increase). At this stage the cell was losing performance at rate of 1,000 mV/kh. Similar voltage changes and related degradation rates at the initial stage (<100 h) were observed for other cells. **Table 5** summarized the obtained results.

	Test	Initial Voltage	Voltage @100 h	$\Delta V_{0-100 \ h}$	Degradation _{0-100 h}	
n	umber	mV	mV	mV	mV/kh	%/kh
(Cell 1	873	1,005	132	1,320	151
(Cell 2	955	1,000	45	450	47
	Cell 3	1,032	1,118	86	860	83
(Cell 4	1,059	1,198	139	1,390	131
	Cell 5	972	1,094	122	1,220	126

Table 5. The voltage change and degradation rate observed for various cell samples during the first 100 h of the electrolysis operation with steam on both cells electrodes

After rapid logarithmic-like growth of the cell voltages the voltage change started to slow down. In case of the Cell 5 between 100 h to 200 h of the long-term test only 46 mV voltage rise was recorded. The degradation rate for this period was 460 mV/kh (42 %/kh). Results for other samples are presented in **Table 6**. Gradually the trend changed into a linear growth and from approx. 200 h was steadily increasing till the end of the test. During the last 800 h voltage increased to 1,308 mV (176 mV rise). The degradation rate for this period reached 220 mV/kh, 19%/kh. Similar behaviour was observed for almost all samples. Overall voltage change for cell 5 during the 1,000 h test amounted 329 mV what constitute a 34 %/kh degradation rate.

Table 6. The voltage cl	anges and degradation	rate observed for	various cell sa	mples between
100 h and 200 h of the e	electrolysis operation w	vith steam on both o	electrodes	

Test number	Voltage @200 h	$\Delta V_{100-200~h}$	Degradati	ON 100-200 h
	mV	mV	mV/kh	%/kh
Cell 1	1,051	46	460	46
Cell 2	1,037	37	370	37
Cell 3	1,167	49	490	44
Cell 4	1,245	47	470	39
Cell 5	1,140	46	460	42

Gradually the voltage degradation trend changed into linear growth and from approx. 200 h was steadily increasing till the end of the test. During the last 800 h voltage increased to 1308 mV (176 mV rise). The degradation rate for this period reached 220 mV/kh, 19%/kh. Similar

behaviour was observed for almost all of the samples (**Table 7**). The overall voltage changes for cell 5 during the 1,000 h test amounted 329 mV what constitute a 34% /kh degradation rate.

Test	Max Voltage	Degrada	l tion >200 h	Overall degradation	
number	mV	mV/kh	%/kh	mV/kh	%/kh
Cell 1	1,051 @ 200 h	n/a	n/a	890	102
Cell 2	1,299 @ 1,000 h	328	32	344	36
Cell 3	1,300 @ 600 h	333	28	447	43
Cell 4	1,282 @ 350 h	247	20	637	60
Cell 5	1,301 @ 1,000 h	201	18	329	34

Table 7. The maximum voltage and overall degradation rate observed for various cell samples during the electrolysis operation with steam on both electrodes

The conducted long-term test revealed the high voltage increase during the operation under with steam as a anodic sweep gas. The overall test trend of voltage change was similar. The rapid initial voltage rise and gradual change to the linear growth. This behavior implies some serious degradation mechanism taking place in these conditions. For deeper understanding of the observed degradation phenomena during the long-term operation of the SOC the test with Cell 5 was carefully prepared, and additional electrochemical tests were conducted.

4.1.3. General electrochemical analysis of the Cell 5

To understand the behaviour of the investigated cell in new operating conditions it is important to measure and investigate the initial state and parameters, as well as to explain the influence of sweep gas change during electrolysis operation. In order to track all of the substantial processes, it is necessary to determine the starting cell conditions and compare them to after test status. The scheme of the methodology of electrochemical analysis is presented in **Figure 51**.



Figure 51. Methodology of the electrochemical measurements

For proper preliminary characterization of the cell with a use of the impedance spectra three types of sweep gas was used: air, steam, nitrogen, and its mixtures.

Analysis of the anodic compartment sweep gas influence on cell polarization

The general influence of various sweep gases on the cell behaviour during electrolysis operation can be observed in the polarization curves in **Figure 52**. For all of the cases the cathode flow was fixed to 300 Nml/min and gas composition was 30 vol. % H₂ and 70 vol. % H₂O. The anode flow was kept at 500 Nml/min and different types of sweep gas was used to determine the cell behaviour. The OCV when air is supplied to the anode side is higher (917 mV) than when nitrogen (782 mV) or steam (792 mV) is used.



Figure 52. Polarization curve of the investigated Cell 5, operated in electrolysis mode under various sweep gas configuration.

The shape and slope of polarization curves for air and nitrogen cases are similar, however the voltage - current relation when steam is used as a sweep gas is more steep. This indicates that the polarization of the cell is higher when operated in these conditions. Based on the linear part of the curves the area specific resistance was calculated and amounted 275 m Ω cm² in case of air. For nitrogen ASR reached 322 m Ω cm² and for steam 409 m Ω cm².

Impedance spectroscopy measurements for various sweep gases

For further analysis the impedance spectrometer was used to measure the spectra under changing sweep gas conditions. EIS measurements were conducted with the use of Zahner Zennium spectrometer and potentiostat under constant current density of -0.25 A/cm² (constant current load of 4 A). The data was gathered in frequency range of 7.5 mHz-112 kHz and 220 frequency samples for each spectrum. The initial spectra were obtained for various sweep gases before long-term degradation measurements. The results are presented in form of Nyquist plot in **Figure 53**.



Figure 53. Impedance spectra of the investigated Cell 5, operated in electrolysis mode (-0.25 A/cm^2) under various sweep gas composition.

It should be notice that in case of air and air/nitrogen mixtures the obtained spectra have a similar shape. The intersection with real axis at high frequencies and two characteristic arcs are very similar. However, in case of just pure nitrogen operation the polarization of the cell increased substantially and when steam was added to the anode side the impedance spectra was both shifted and extended what suggest polarization and ohmic resistances increase. Based on the equivalent circuit model [135] the data was fitted and even with some low-frequency distortion found in data the models demonstrated good quality of the approximation (**Figure 53**) and ohmic as well as polarization resistance have been established. The comparison of the results for various cases is presented in **Table 8**.

Anode gas composition [vol. %]	$R_p [\Omega \ cm^2]$	$\mathbf{R}_{\Omega} \left[\mathbf{\Omega} \ \mathbf{cm}^2 \right]$
100 air	0.138	0.133
50/50 air/N ₂	0.149	0.135
100 N ₂	0.225	0.138
50/50 air/H ₂ O	0.176	0.151
100 H ₂ O	0.269	0.168

Table 8. Comparison of the ohmic resistance and cell polarization under various sweep gas configuration.

The ohmic resistance was found to be very similar in all cases with air and air/nitrogen mixtures. However, the steam content in the oxygen electrode space clearly leads to increase in ohmic resistance. The polarization resistance of the cell is also found to be highly influenced by steam, but in this case also low oxygen sweep gas (100% nitrogen) was found to highly increase the polarization.

DRT analysis of impedance spectra for various sweep gases

The EIS measurements were used for further analysis of the distribution of relaxation times with a use of in-home software. Program is written in C++, with optimized open source math libraries [136, 137, 138] and allowed to calculate distribution of the relaxation time using algorithm proposed by Saccoccio [139]. This method allows further analysis of the degradation phenomena, and differentiation of physio- electrochemical processes with different characteristic time constants. The detailed description of the DRT theory can be found elsewhere [140]. The obtained results for the different sweep gas and gas composition at each electrode are presented in **Figure 54**. The change of the DRT peaks under different gas composition can help in identification of phenomena that are taking place at the SOC operated in electrolysis mode.



Figure 54. DRT analysis and comparison of air, N_2 and steam used as a sweep gas and fuel electrode sensitivity to composition change

The spectra revealed six prominent peaks arranged in 3 groups of peaks: P1 at high frequency triad (P2)-(P4), and one or two peaks (P5) and (P6) at lower end of spectrum. Each of the peaks can be attributed to different processes and impedances in the analysed cell. According to [127,141, 142] the low frequency peak at 1-10 Hz (P6) can be associated with gas conversion and gas diffusion in oxygen electrode pores. Peak at 20-50 Hz (P5) is connected to oxygen-surface exchange (gas diffusion) and oxide ion transfer resistance in oxygen electrode. In the frequency range from 100 to 1,000 Hz some secondary peaks (P4) can be found that are linked to fuel and oxygen electrode transport. Here P4 strongly reacts to the sweep gas change at oxygen electrode, but not that much in case of fuel electrode gas change. Peaks P3 that are present at frequencies above 1 kHz are considered to be responsible for the resistance of charge transfer mainly from fuel electrodes. It was reported that at frequencies between 5000 and 10 000 Hz the increase of the impedance can be associated with degradation of nickel triple-phase boundary [143]. In case of the higher frequency peaks >10 kHz there is no consensus about their association, but it was suggested that it might be related to solid-solid oxygen

electrode transfer processes or loses on the current collector at oxygen electrode [141]. The suggested contributions and peak identification gathered from the literature are presented in the **Table 9**.

	P1	P2	P3	P4	P5	P6
Expected frequency range	60-80 kHz	8-10 kHz	1-5 kHz	100-1,000 Hz	10-80 Hz	1-10 Hz
Associated with process	Not clear, linked to solid-solid oxygen electrode transfer processes or loses on the current collector at oxygen electrode side	Oxide ion transfer resistance attributed to oxygen and fuel electrode	Fuel electrode charge transfer	Secondary peaks (fuel and oxygen electrode transport)	Oxygen- surface exchange and oxide ion transfer resistance in the oxygen electrode and gas diffusion	Gas conversion and gas diffusion

Table 9. Possible DRT peaks attribution [127, 141, 144]

The variation of the sweep gas and fuel electrode gas composition showed that the modest change of N_2/O_2 proportion in the sweep gas have limited influence on the processes. However, when pure nitrogen or pure steam is involved the impact on the cell response is clear. In case of pure nitrogen additional peak (P6) was identified in low frequency part. Additionally the summits of peaks P1 and P2 was shifted to lower frequencies. For measurements when only steam is used as a sweep gas the low frequency processes are more affected by. The surface under P5 rose substantially and additional process P4 was identified. Also, some peaks (P1, P2) were shifted to higher frequencies. In case of fuel electrode gas composition variation some minor changes in P3 peak were found.

Impedance spectra measurements during long-term operation

In order to gather more information concerning the degradation phenomena observed in longterm cell operation during long-term degradation measurement of the Cell 5, sixteen impedance spectroscopy measurements were performed (approx. every 60 h). The cell response was measured and some of the obtained data are presented in form of a Nyquist graph in Figure 55.



Figure 55. Evolution of impedance spectra during long-term measurement of cell 5; Current density -0.25 A/cm². CFG: 70% H₂O / 30% H₂; ASG: 100% H₂O

It was found that the shape of arcs and position of the spectra is significantly changing with time. The shift of the intersection with real axis points out that the cell resistance is rising when the cell is kept in high steam content conditions at anode side. The change of the arcs shape and size implies the change of the cell polarization resistance. Analysis of the spectra by fitting to the equivalent circuit model allowed to separate polarization (r_p) and ohmic (r_{Ω}) resistances. The evolution of the resistances during the long-term cell run are shown in Figure 56.



Figure 56. Ohmic resistance and cell polarization change during long-term measurement of Cell 5; Current density -0.25A/cm². CFG: 70% H₂O / 30% H₂; ASG: 100% H₂O

During 1,000 h operation substantial change in the polarization and ohmic resistances was found. This is especially recognized in the first stage (first 200 h) of the long-term operation where the polarization increases from 0.269 Ω cm² to 0.628 Ω cm². After this initial period the rate of resistance slowed down and linearly increased till the end. The value of ohmic resistance at the start was lower than polarization resistance and it amounted 0.168 Ω cm², however during the long-term measurements the ohmic resistance rise faster and after 1,000 h the resistances almost leveled with final values 0.686 and 0.632 Ω cm². The change of the resistances directly corresponds to the voltage increase during long-term operation where significant voltage increase at initial phase was found followed by linear voltage degradation.

DRT analysis of impedance spectra during long-term operation

In order to distinguish individual degradation processes characteristic for different relaxation times the EIS data sets were treated using DRT. The results obtained from EIS taken at different times of the degradation measurement are compared in Figure 57 (initial stage) and **Figure 58** (after 1,000 h duration)



Figure 57. DRT analysis for initial 309 h of long-term cell 5 measurement; Current density - 0.25A/cm². Flow composition cathode: 70% H₂O / 30% H₂; anode: 100% H₂O

At the start of the measurements the DRT analysis allowed to distinguish five apparent peaks. However during first hours of operation with steam as a sweep gas the sixth peak P6 was identified at low frequency range. This peak in the initial stage (< 200 h) was characterized by fast growth and then gradually reached maximum hight at approx. 300 h. Along with high P6 rise peak P5 was decreasing. It looks like some kind of trade-off between two processes. Additionally, the summit and shape of P1 and P2 were extended and shifted to higher frequencies. P3 and P4 after initial change did not evolve much with time.



Figure 58. DRT analysis for long-term cell 5 measurement; Current density -0.25A/cm². Flow composition cathode: 70% $H_2O / 30\% H_2$; anode: 100% H_2O

Again, after 300 hours of operation the P1 and P2 were gradually rising, but without further frequency shift. However, P6 after its fast growth started to fall back and slowly merging with P5 (in the last measurement 1,006 h it looks like the P6 elapsed totally).

During the initial stage the most affected processes P1, P2 and P6 according to **Table 9** are related to the oxide ion transfer resistance, gas diffusion processes and oxygen surface exchange. This may suggest that the bulk diffusion and microstructure (porosity, tortuosity and/or surface area) were somehow influenced by steam.

Performance comparison before and after the long-term of degradation measurements

After long-term operation of the SOC cell under electrolysis mode with a steam as a sweep gas the performance of the cell were once again measured with I-V and EIS measurements. The flow conditions were reproduced from the initial measurements and the obtained results were compared with the values measured before long-term degradation evaluation. In **Figure 59** and the polarization curves and impedance spectra measured with the cell operated with steam (top) and air (bottom) are compared. The results show a significant change of the curves and spectra shape and values indicating severe perdormance drop. However, the OCV values before and after long-term test are exactly the same what shows that the tightness level of the cell and system setup was stable and that no leakage problem was triggered during the test duration. The I-V analysis showed the considerable decrease in cell performance. The initial voltage measured for steam as a sweep gas at -0.25 A/cm² was 976 mV. After degradation test it increased substantially to 1,315 mV. The average degradation rate calculated for these conditions reached 336 mV/ 1,000 h (34.7 %/1,000 h). Similar degradation rate of this cell was calculated for measurements performed with air before and after long-term degradation measurement. At the beginning voltage at -0.25 A/cm² was 985 mV, but at the end of the cell operation at the same current load cell voltage reached 1,297 mV. Hence the average degradation rate calculated for this case was 312 mV/1,000 h (31.6 %/1,000 h).

Similar drop in the cell performance was found on the impedance spectra where ASR of 0.271 Ω cm² was followed by 1.291 Ω cm² post degradation test. The average ASR degradation rate was found to be 1.02 m Ω cm²/ 1,000 h.



Figure 59. Comparison of the polarization curves (left) and impedance spectra (right) of the investigated Cell 5 operated in electrolysis mode, measured before and after long-term degradation test. H_2O as a sweep gas -top; air as a sweep gas – bottom)

In the polarization curves performed after long-term degradation measurements, a much lower currents can be supplied to the cell. At 1.35 V maximum current obtained before was 18 A and 20 A for steam and air, respectively. After 1,000 hours operation with steam only 4 A could be reached.

4.1.4. *Post mortem* microstructural analysis

The cell after long-term operation was dismantled from the test section (**Figure 60**). No visible cracks or severe LSCF delamination was observed. Small samples of the cell were prepared for further microstructural investigation.



Figure 60. Photo of the housing and cell after the long-term operation (top left - oxygen electrode side; top right – fuel electrode side after dismounting; bottom left- golden interconnect; bottom right - housing before disassembly).

In **Figure 61.** SEM image of the cell 5 cross-section after 1000 h degradation test under -0.25 A/cm^2 current with H₂O as sweep gas. Visible layers delamination top left - GDC/electrolyte, top right - LSCF electrode delamination from new interlayer, bottom left the SEM images of the cell 5 were presented. The functional layers are well-adhered to each other and the porous microstructure of the both electrodes is maintained without any significant changes. Small cracks perpendicular to the electrolyte surface were found in oxygen electrode, however they might be and effect of the cell disassembly from the interconnector. In addition, the new intermediate layer between the air electrode and GDC barrier layer was formed. It is visible as a brighter area near the white GDC boundary. The new layer is danse and has thickness of about

 $4 \ \mu m$. In addition, noticeable delamination of both the barrier layer and the oxygen electrode were found.



Figure 61. SEM image of the cell 5 cross-section after 1000 h degradation test under -0.25 A/cm^2 current with H₂O as sweep gas. Visible layers delamination top left - GDC/electrolyte, top right - LSCF electrode delamination from new interlayer, bottom left -zoom at the interphase of air electrode – GDC – electrolyte – fuel electrode

Similar observation were noticed also in Type A cells. **Figure 62** presents the cross-section of the sample cell 3 after long term degradation test in steam. The creation of new dense interlayer was also found.



Figure 62. SEM image of the cell 2 cross-section after the long-term degradation test with H_2O as sweep gas

In order to identify the elements composition of this sub-layer the EDS analysis was performed. The EDS map of the electrolyte/GDC/oxygen electrode region is presented in **Figure 63**. Non-homogenous distribution of the Sr cations in the electrode can be seen with aggregation in the top of the layer and nearby the GDC layer. However, no diffusion of strontium through the barrier layer into the electrolyte was observed. Moreover, Y and Cr accumulation can be noticed nearby this region. The Cr has been detected in the whole volume of electrode implying that steam pronounced chromium volatilization from the steal part of test rig.



10µm

Figure 63. SEM/EDS map analysis image of the cell cross-section after the long-term degradation test of cell 5.

The more detailed analysis, with selected EDS spectra is gathered in **Figure 64**. The measurements of the specific region of the cell cross-section allowed comparison of the composition change along the oxygen electrode. The results points out that operation in the high humidity environment influences the stability of the oxygen electrode. Based on the EDX scan analysis changes of the cations content along the cell cross section are presented in **Figure 64**.



Figure 64. EDS scan of the cell 5 cross-section after long-term degradation test.

The results shows that the Sr content is changing through the air electrode. The Sr migration to the top layer and pronounced migration towards the GDC layer were found. The highest Sr content was detected near the barrier layer. On SEM image visible as a new darker layer in the electrode. It should be also noticed that in this area the ratio between La and Sr is close to 1 what suggest the formation of the new phase.

Moreover, slight depletion of the La at the top region can be noticed and presence of Cr was detected. Chromium was present in the whole volume of the air electrode with the highest atomic share at the formed sublayer between GDC air electrode.

The composition changes in oxygen electrode and element migration suggests at least partial decomposition of the oxygen electrode material. In order to further confirm this founding the XRD measurements were performed and results are presented in **Figure 65**.



Figure 65. XRD analysis of cell 5 after 1000 h test and reference pristine cell with LSCF electrode.

It is clear that significant distortion of the material structure took place. Sample operated in high steam content during long-term experiment showed in XRD pattern many new phases created in the oxygen electrode. The symbol "?" de-notes the most significant reflexes of the novel phases. Additionally, the microstructure of the fuel electrode was also investigated. **Figure 66** presents the SEM/EDS analysis of the representative part of the fuel electrode after long-term experiment.



Figure 66. SEM/EDS map analysis image of the fuel electrode after the long-term degradation test of cell 5.

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	1898	9.12	9.81	27.32	1.85	20.24
Oxygen	8	8435	18.47	19.88	41.56	2.72	14.72
Calcium	20	1701	1.32	1.42	1.18	0.09	7.17
Iron	26	345	0.62	0.66	0.40	0.11	17.30
Nickel	28	7825	21.11	22.71	1 <mark>2.</mark> 95	0.75	3.57
Zirconium	40	45733	34.63	37.27	13.67	1.34	3.86
Lanthanum	57	803	1.27	<mark>1.37</mark>	0.33	0.15	11.64
Yttrium	39	8298	6.40	6.88	2.59	0.32	<mark>4.9</mark> 3
		Sum	92.92	100.00	100.00		

Table 10. EDS analysis results for representative part of fuel electrode region.

The microstructural analysis of fuel electrode revealed no nickel agglomeration or depletion effects present in the tested sample.

4.1.5. Discussion

4.1.5.1. Electrochemical measurements

During the electrochemical analysis the 5 different solid oxide cell samples were operated in electrolysis mode with steam used as a sweep gas on the oxygen electrode side for more than 3000 h. It was found that long-term operation of SOC in these conditions under moderate current loads (\leq -0.25 A/cm²) leads to rapid voltage increase and irreversible performance loss. In all of the tested samples the degradation rate exceeded 30 %/kh. In all of cases the initial period up to 200 h exhibit the highest degradation rate when voltage growth was logarithmic. The character of changes may imply some severe morphological changes in the cell materials. Gradually the voltage growth trend changed into linear growth and voltage steadily increased after that till the end of the measurements. In order to identify the potential source of the high degradation rate the cell 5 was subjected to through electrochemical analysis.

In the first step the influence of various sweep gases (N_2 , Air, H_2O) on the cell general characteristics during electrolysis operation was compared. Apart from obvious differences in OCV, the shape and slope of polarization curves for air and nitrogen cases were found to be similar at higher current loads. This behaviour is expected since the atmospheres are of the same nature. However, when steam was used as a sweep gas the voltage - current density relation was more steep. Bigger discrepancies are clear at higher current densities, but still at the initial

stage cell was able to perform quite well and reach current density of almost 1.2 A/cm^2 at a voltage below 1.4 V.

The ASR calculated for each case showed noticeable differences: 0.275 Ω cm² in case of air, 0.322 Ω cm² for nitrogen and 0.409 Ω cm² for steam. The ASR values obtained from i-V curves ware confirmed by EIS analysis. When air and air/nitrogen mixtures were used the measured impedance spectra had a similar shape. Steam content in the sweep gas led to minor increase of the ohmic resistance (0.138-0.168 Ω cm²) and had even higher influence on the cell polarization. The impedance spectra were both, shifted and extended, and polarization reached 0.269 Ω cm² in comparison to 0.138 Ω cm² for air. The cell polarization when operated in 100% nitrogen was also high 0.225 Ω cm². This observation suggests that higher cell polarization when operated in lower oxygen containing gases may be caused by increase of oxygen non-stoichiometry in LSCF [145]. This non-stoichiometry is often followed by 2-5 time decrease of total conductivity [146,147] and sufficient decline of the oxygen mobility, both, bulk chemical diffusion and surface exchange coefficient [146]. Later ones are considered as crucial parameters, which govern electrochemical activity [148]. This effect may be less visible when electrode operated at higher anodic current densities, when released oxygen partially compensated its deficiency in sweep gas.

After preliminary characteristic of the Cell 5, the sample was operated in galvanostatic conditions for over 1,000 h. The frequent impedance measurements showed that the shape and position of the impedance spectra were evolving during the long-term operation. Data analysis revealed high polarization and ohmic resistance changes especially in the early stage (first 200 h) of the operation.

The long-term measurements of the Cell 5 were concluded by the second investigation of cell performance. Results were compared to the ones obtained before long-term exposure to high steam concentration at oxygen electrode side. The ASR calculated from the linear part of the obtained polarization curves and independenly from impedance spectra shows 3-4 times resistance increace. The ASR comparison results are shown in **Table 11**.

Sweep gas on the anode side	Measurement before or after long-term degradation test with steam	ASR calculated from linear part of polarization curve [Ω cm ²]	ASR calculated from impedance spectra [Ω cm ²]
Steam	before	0.416	0.437
Steam	after	1.314	1.318
Air	before	0.275	0.271
	after	1.292	1.291

Table 11. Comparison of the ASR calculation results before and after long-term of degradation measurements with steam.

In search of the degradation mechanism DRT analysis identified six apparent peaks related to various processes. The most visible changes were found for the peaks at high frequency range 10-90 kHz (P1, P2) and at lowest frequencies 1-10 Hz (P6). Peak P6 related to the gas diffusion in oxygen electrode pores, during initial stage rise significantly, however after 300 h the peak area start to fall back. This strange evolution in the DRT pattern is quite unique. It suggests that the resistance related to the diffusion rise at first, but later it gradually decreased its influence on the cell performance. This behaviour may be explained by the creation of the dense high Sr containing interlayer that highly influenced the diffusion processes. However during the experiment, the LSCF material decomposed into various phases and this could possibly change the oxygen electrode process mechanism. For example via shifting of oxygen transfer from surface path to bulk path (due to the TPB active sites reduction at OE)[149]. It is considered that due to formation of the interlayer and the severe decomposition of the LSCF material the oxygen electrode processes evolved and were less influenced by the diffusion process in the second part of the degradation experiment. Additionally, the slow decrease of P5 amplitude especially in the first stage of the experiment suggest that the gas surface exchange process were somehow promoted at the oxygen electrode or it was some kind of tradeoff between two processes (P5 and P6) as mentioned above. Similar changes within the low frequency peaks were observed in [150].

In case of high frequency peaks (P1 and P2) the initial frequency was shifted toward even higher frequencies and then the peaks gradually rise and expand. At this time constants the processes typically linked to charge and oxide ion transfer in the mixed ionic-electronic oxygen electrode are registered. The crippling of the charge and ionic conduction process and resistance increase is likely caused by de-mixing of LSCF material (cation migration and mixing). The new

creation of many secondary phases revealed in XRD spectra may explain the observed resistance increase at high frequencies.

It should be noted that qualitative degradation of the oxygen electrode was concluded during first 300 h of the experiment. During this phase the DRT pattern have changed significantly implying that LSCF decomposition influenced many processes taking place in the cell. The cell performance decline in the second stage of the was more quantitative and might be described as a growth of resistivities related to ohmic loses and P1-P2 processes. The fallback of the resistivity related to P6 may be associated with the morphological and microstructural changes that took place in the cell anode. Initially the P6 rise quickly within first 300 h, but after the electrode decomposition the character of the process changed and the share of the resistivity coming from P6 decreased. However deep analysis would require separated studies.

4.1.5.2. Structural and morphological changes in LSCF anode

The post mortem analysis of the sample exposed to electrolysis operation in high content of steam revealed clear morphological changes in the oxygen electrode material. SEM evaluation reported many structural defects present. The tangential cracks and layers delamination strongly limits the active surface of cell. This leads to development of both, ohmic and polarization resistance. The cracks formation and layer delamination may have its origin in crippling of the oxygen ion conductivity by chemical degradation of the electrode material and what in consequence leads to excessive pressure of the oxygen [108]. The delamination process does not demonstrate a tendency to fade out during the operation in the galvanostatic mode, what may explains the steady, almost linear rise of the ohmic resistance of cell (**Figure 56**).

The performed EDS analysis suggests instability of the LSCF based electrode in high steam content atmosphere, especially close distance to the barrier layer where the majority of the oxygen evolution reactions takes place. This behavior explains the rising ohmic and polarization resistance of the cell found during long-term operation. The results imply that the high concentration of steam on the LSCF electrode causes some instability of the material/its properties (chemical corrosion). That phenomena decreases the electrode ionic conductivity causing the cell performance to drop drastically. Interlayer containing elevated amount of strontium implies its separation from the perovskite lattice what leads to the loss of electronic and ionic conductivities. The strontium separation is known phenomena that occurs above 600

 $^{\circ}$ C [151]. According to [152] strontium precipitation in form of SrO or SrO₂ is realized by mechanism that is related to oxidizing conditions or oxygen vacancies (LSCF even in oxidizing conditions is characterized by high oxygen vacancy buildup). The formation of Sr-O compound that takes place on the LSCF surface can be written as:

$$Sr_{(La)} + 0.5 \ O_{2(g)} \to SrO_{(s)} + V_{(la)} + 2h$$
 (Eq. 43)

$$Sr_{(La)} + 0.5 \ O_{2(g)} + O_o^x \to SrO_{2(s)} + V_{(la)} + V_o^{"}$$
 (Eq. 44)

The crystalline structure was analysed by XRD measurements. It revealed presence of the many new phases but exact compounds were not identified due to large number of registered peaks and poor formation of the crystal lattice in products of the decomposition. However Sr accumulation always involves surface phase separation [153], because of limited excess of SrO in cubic perovskite structure. It is expected that the rest of additional SrO forms interlayers in a bulk lattice in form of structurally reconstructed phase often referred to as the Ruddlesden-Popper (RP) phase [154]. Nevertheless heterogeneous LSCF structure and creation of this Sr oxides contributes to the increased resistance and lower cell performance [155].

Another aspect is the specific conditions that were present on the oxygen electrode side. Both, high steam content and anodic polarization may be the factor in LSCF material decomposition rate. The presence of steam enables further reaction with precipitated SrO and formation of hydroxide such as Sr(OH)₂.

$$SrO_{(s)} + H_2O_{(g)} \to Sr(OH)_{2(g)}$$
 (Eq. 45)

This compound can be desorbed from the surface and in gaseous form can migrate throughout pores in oxygen electrode and GDC layer. Typically strontium hydroxide migrates towards electrolyte where it can react with Zr and form dense SrZrO₃ structure inside pores of the barrier layer.

$$Sr(OH)_{2(g)} + Zr_{Zr}^{x}(YSZ) + 2O_{o}^{x}(YSZ) \rightarrow SrZrO_{3} + H_{2}O_{(g)} + 2V_{o}^{"}(YSZ) + V_{Zr}(YSZ)$$
(Eq. 46)

However, in the analysed samples no strontium agglomeration was found near the electrolyte, but the mechanism of Sr migration may explain the creation of discovered interlayer on GDC-LSCF interface. This would suggest that the steam acts as a stimulant and accelerate the migration of Sr and depletion of LSCF and other created phases, by reacting with SrO. Also [156] reported high impact of steam on Sr segregation in comparison to oxygen and air atmospheres, but states that full mechanism of this phenomena is still not established but it is clearly influenced by the gas atmosphere and microstructure. Also the anodic polarization may influence LSCF decomposition by local saturation of the oxygen atoms [120]. This in consequence may contribute to the LSCF deterioration according to reaction:

$$Sr_{(La)} + O_o^x \to SrO_{(s)} + V_{(La)} + V_o^{"}$$
 (Eq. 47)

Discovered high LSCF chemical corrosion and formation of Sr-O compounds certainly leads to increased ohmic resistance since most of these compounds (e.g. SrO and Sr(OH)₂) are dielectrics [153]. However, the creation of the new dense interlayer could influence the diffusion process what was also one of explanation for the degradation found in electrochemical measurements.

Another factor that might influenced the electrochemical performance of the cells is presence of chromium that was found in the volume of LSCF electrode. It has been reported that gaseous chromium oxide CrO₃ may easily react with segregated SrO via four reactions [157]:

$$SrO_{(s)} + CrO_{3(g)} \rightarrow SrCrO_{4(s)}$$
 (Eq. 48)

$$SrO_{(s)} + CrO_{3(g)} \to SrCrO_{3(s)} + 0.5 O_{2(g)}$$
 (Eq. 49)

$$SrO_{(s)} + \frac{2}{3}CrO_{3(g)} \to \frac{1}{3}Sr_3Cr_2O_{8(s)} + \frac{1}{6}O_{2(g)}$$
 (Eq. 50)

$$SrO_{(s)} + \frac{1}{2}CrO_{3(g)} \rightarrow \frac{1}{2}Sr_2CrO_{4(s)} + \frac{1}{4}O_{2(g)}$$
 (Eq. 51)

Additionally, chromium in presence of water vapour more commonly exist in form of volatile oxyhydroxite $Cr(OH)_2O_2$ [158] Since perovskite easily interacts with chromia compounds various secondary phases are usually formed that inhibits the oxygen evolution and thus have an impact on the overall cell performance. This reported chemical interaction of the LSCF with steam, in conjunction with de-mixing and Sr segregation may explain the observed complicated polarization change of the cell (**Figure 56**).
4.2. Operation of the SOC cell under electrolysis mode with nitrogen as a sweep gas

4.2.1. Objectives

Due to the high degradation rate found during SOC operation with steam as ASG it is necessary to gather data for the reference conditions. Typically reference gas is usually air, however, since the steam has a low oxygen content the reference gas was chosen to be nitrogen. This approach will allow to search other degradation processes that may be related to low oxygen content in the sweep gas.

4.2.2. Cell performance during long-term operation with nitrogen as a sweep gas

The long-term operation of SOC cells with nitrogen used as a sweep gas was performed in order to compare the degradation rates to the ones obtained with a steam. The same two types of cells were measured in two independent experiments. During the long-term measurements the cells were operated in electrolysis mode under constant current of 4 A. The cathode gas composition constituted 70 vol. % steam and 30 vol. % hydrogen. On the side of oxygen electrode only nitrogen was supplied (**Table 12**).

Table 12. Index of long-term measurements of S	SOEC operated with nitrog	gen as a sweep gas
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Experiment	Duration	Cell	Current load	Anode		Cat	hode
Identifier	[h]		[A]	Flow [mNl/min]	Composition [vol. %]	Flow [mNl/min]	Composition [vol. %]
Cell 6	1,061 h	Type A	4A	500 N ₂	100 N ₂	$170 H_2 + 400 H_2O$	70 H ₂ O
Cell 7	1,000 h	Type B	4A	500 N ₂	100 N ₂	$60 H_2 + 140 H_2O$	70 H ₂ O

When initial characterization of cells were finalized the samples were stabilized at nominal current load of 4 A in standard sweep gas conditions (air). When stable operating temperature and voltage was reached the nitrogen was gradually introduced and air flow was stopped. The cells operated under this conditions for 1,000 h. The cell voltage evolution during the long-term operation with nitrogen was recorded and is presented in **Figure 67**.



Figure 67. Voltage evolution during long-term measurements of Cell 6 and Cell 7; Current density -0.25 A/cm^2 . Flow composition C: 70 vol. % H₂O/ 30 vol. % H₂; A: 100 vol. % N₂

For both types of the cells the observed voltage change during the long-term operation was found to be much lower in comparison to the cells operated with steam as a sweep gas. In case of Type A cell the voltage rise 12 mV during 1061 h operation. This corresponds to the 11.3 mV/kh degradation rate. Similar values were found during long-term measurement of type B cell where degradation rate amounted 11 mV/kh. The degradation values are summarized in **Table 13**.

Table 13. The overall degradation rate observed for various cell samples during the electrolysis operation with nitrogen as a seep gas on oxygen electrode

Test number	est Starting Max Voltage		Overall degradation	
	mV	mV	mV/kh	%/kh
Cell 6	923	935 @ 1061 h	11.3	1.22
Cell 7	900	911 @ 1,000 h	11	1.2

The results obtained during long-term measurements with nitrogen as a sweep gas shows that the degradation rate is much lower than was found during operation with steam at the oxygen electrode side. In order to properly compare the results similar electrochemical test were conducted for the Ccell 7 and are presented in the next chapter.

4.2.3. General electrochemical analysis of the Cell 7

In order to compare the results the similar methodology of electrochemical analysis as in case of the Cell 5 was implemented. Methodology was presented in **Figure 51**, however, in this case, the nitrogen was used as a sweep gas during 1,000 h cell operation under galvanostatic conditions -0.25 A/cm^2 .

Analysis of sweep gas oxygen content depletion on polarization curves

The influence of gradual change of sweep gas from air to nitrogen during electrolysis operation is presented in **Figure 68**. For all cases the CFG was fixed to 200 Nml/min and gas composition was 30 vol. % H_2 and 70 vol. % H_2O . The anode flow was kept at 500 Nml/min and different nitrogen mixtures were used to determine the cell behaviour.



Figure 68. Polarization curve of the investigated Cell 7, operated in electrolysis mode under various sweep gas configuration.

The shape and slope of polarization curves for air and air/nitrogen mixtures are very similar. In case when only nitrogen is used the initial voltage is lower (768 mV) then when air is supplied to the anode side (894 mV), but at the higher current densities the character of the I-V relation is similar to air and air/nitrogen mixture.

Impedance spectroscopy measurements for various oxygen content in sweep gas

Further electrochemical analysis involved the impedance spectroscopy measurements that were taken for various oxygen content in sweep gas. The results are presented in form of Nyquist plot in **Figure 69**.



Figure 69. Impedance spectra of the investigated Cell 7, operated in electrolysis mode (-0.25 A/cm^2) under various oxygen content in sweep gas.

The results of the initial performance of the cell gathered during measurements of sample seven are similar to the ones obtained for the Cell 5 and shows that for air and air/nitrogen mixtures the shape and intersection with real axis at low frequencies are comparable (only small increase of the polarization is visible). When the pure nitrogen is introduced to the oxygen electrode side the polarization of the cell rise essentially. Base on the equivalent circuit model the data was fitted, allowing to determine ohmic and polarization resistance. The results are presented in **Table 14**.

Table 14. Comparison of the ohmic and polarization resistance of the Cell 7, operated in electrolysis mode (-0.25 A/cm^2) under various oxygen content in sweep gas.

Anode gas composition	$R_p \left[\Omega \ cm^2\right]$	$R_{\Omega} [\Omega \ cm^2]$
Air	0.108	0.127
50% Air/50% N ₂	0.121	0.130
100 % N ₂	0.193	0.137

The values of the resistances obtained here are comparable to the ones found for the Cell 5 what confirms the cell measurement reproducibility and it allows further long-term analysis.

DRT analysis of impedance spectra for various oxygen content in sweep gas

The impedance spectra results were used in order to calculate the distribution of relaxation times. The DRT analysis for various sweep gas is presented in **Figure 70**.



Figure 70. DRT analysis and comparison sweep gas and fuel electrode sensitivity to composition change of the Cell 7.

The DRT analysis identified five prominent peaks. They were named according to the frequencies presented earlier in **Table 9**. When air and air/nitrogen mixture is used, there is only some minor changes in peak P5 and P6 which are related to the oxygen surface exchange and gas conversion/gas diffusion. However, when 100% nitrogen is used as ASG the change amongst the peaks is more pronounced. Peak P6 rise substantially while P5 drop down. Also, triad (peaks P4 and P3) noticed some minor changes and its summits were shifted in frequencies.

Impedance spectra measurements during long-term operation with nitrogen as a sweep gas

During the long-term operation of the Cell 7 in electrolysis mode (-4 A) with a nitrogen as a sweep gas several impedance spectroscopy measurements were performed. Some of the selected data are presented in form of a Nyquist graph in **Figure 71**.



Figure 71. Evolution of impedance spectra during long-term measurement of the Cell 7; Current density -0.25 A/cm². Flow composition cathode: 70 vol. % H₂O / 30 vol. % H₂; anode: 100 vol. % N₂

Results shows that shape of arcs is not changing with time however the position of the spectra is somehow shifted. The shift of the first intersection with real axis implies that the cell ohmic resistance is slowly rising during the degradation test with nitrogen as ASG. The spectra were fitted with the equivalent circuit model what allowed to identify the polarization (r_p) and ohmic (r_{Ω}) resistances changes. The evolution of the resistances during the long-term run are plotted in **Figure 72**.



Figure 72. Ohmic resistance and cell polarization change during long-term measurement of the Cell 7; Current density -0.25A/cm². Flow composition C: 70 vol. % H₂O/ 30 vol. % H₂; A:100 vol. % N₂

The measurements taken during 1,000 h operation revealed that there were some minor changes of the polarization and ohmic resistances. The ohmic resistance rise from 0.137 Ω cm² to 0.158 Ω cm² and cell polarization increased from 0.192 Ω cm² to 0.219 Ω cm². The change in resistance values is not high what confirms low degradation rate observed in voltage evolution.

DRT analysis of impedance spectra during long-term operation

In order to obtain the precise view on the degradation and distinguish the processes with biggest impact on the cell performance, the impedance spectra results were further analysed with a use of the DRT. The results obtained at different stage of the long-term cell operation are presented in **Figure 73**.



Figure 73. DRT analysis for long-term the Cell 7 measurement; Current density -0.25 A/cm². Flow composition C: 70 vol. % H₂O/ 30 vol. % H₂; A:100 vol. % N₂

Five independent peaks were identified. However, during the long term operation in the electrolysis mode with nitrogen as a sweep gas only some minor changes between the peaks were found. For P1 frequency shifts and peak area increase were noted. The P3 and P4 also undergo some development, but the overall changes were very moderate. The obtained results are in line with previously presented low degradation of cell performance.

Performance comparison before and after the long-term of degradation measurements

To conclude the electrochemical measurements the I-V curves and impedance spectra were performed and compared to the ones obtained before long-term operation. The results for two different sweep gas cases (air and nitrogen) are presented in **Figure 59**. The ASR was calculated from the linear part of the I-V curves according to the equation 2.24 (Chapter 2.3.2)



Figure 74. Comparison of the polarization curves (left) and impedance spectra (right) of the investigated Cell 7 operated in electrolysis mode, measured before and after long-term degradation test. ASG: air (top), N_2 (bottom);

The difference between measurements taken before and after long-term degradation test are visible on both, I-V and EIS results. The curves registered after are more steep then ones registered before long-term operation. However, the differences found are not significant and the average ASR change calculated for this cases is only 65 m Ω cm². Similar findings were reported for impedance spectra measurements. The EIS spectra for both tested sweep gases exhibited some shifts and minor shape transitions, but calculations based on the equivalent

circuit model showed that only slight changes in ohmic and polarization resistances were found. In Table 15 the comparison of the ASR values before and after long-term operation are presented.

Sweep gas on the anode side	Measurement before or after long-term degradation test with steam	ASR calculated from linear part of polarization curve [Ω cm ²]	ASR calculated from impedance spectra [Ω cm ²]
Nitrogen	before	0.313	0.329
	after	0.381	0.378
Air	before	0.239	0.231
	after	0.302	0.285

Table 15. Comparison of the ASR calculation results before and after long-term degradationmeasurements with nitrogen as a sweep gas of the Cell 7.

Summary of the electrochemical measurements with nitrogen as a sweep gas

The electrochemical analysis covered long-term measurements of two different solid oxide cell type "A" and type "B" in electrolysis mode with nitrogen used as a sweep gas. It was found that long-term operation of SOC under mild current loads (<-0.25 A/cm²) caused only minor voltage increase ~11 mV/kh. Similar findings were recorded during the thorough electrochemical analysis of the Cell 7. The impedance spectra measurements during long-term operation allowed to identify the cell polarization increase of 27 Ω cm² and ohmic resistances raise of 21 Ω cm². DRT analysis did not detected a significant increase of resistance due to any of the identified processes and none additional creation of DRT peaks were found. The comparison on the performance before and after long-term operation with nitrogen as a sweep gas has confirmed the results of low degradation of the cell in this operating conditions.

4.2.4. *Post mortem* microstructural analysis

In **Figure 75** the SEM images of the Cell 7 are presented. The analysis of the microstructure have not found any signs of decomposition, delamination or cracks of functional layers. The oxygen electrode was attached to the GDC layer at the whole length. The electrolyte is dense with a thickness of ca. 4-5 μ m with no visible fractures. In contrast to the samples operated with steam no creation of additional layers were revealed. On the fuel electrode side the porous microstructure with homogeneously distributed pores with diameter below 1-1.5 μ m has been

preserved, however some minor agglomeration of grain has been detected. The layer is well adhered to the support and electrolyte.



Figure 75. Cross-section of the cell 7 after 1000 h test with N_2 as sweep gas: whole cell (top left), interface of air electrode / GDC / electrolyte / fuel electrode functional layer and support (top right), interphase of functional layer of fuel electrode and support (bottom left), zoom at the interphase of air electrode – GDC – electrolyte (bottom right).

Similar findings were confirmed for Type B sample 6. The microstructure of the cross-section after long-term degradation test is presented in **Figure 76**.



Figure 76. Cross-section of the cell 6 after 1000 h test with N₂ as sweep gas.

In case of the Cell 6 electron microscope analysis revealed proper morphology of the cell after long term exposure to electrolysis conditions. The images showed a 4 μ m thick electrolyte and approximately 2 μ m thick GDC layer. No cracks or fractures were found on the interfaces between various cell layers. There are no signs of layers delamination or decomposition. Locally impurities from sealing materials were found.

In order to look for potential material decomposition or elements migration in or between layers the EDS analysis was performed. **Figure 77** presents the data obtained for the Cell 7. Clear element lines that overlap the individual layers were found. Cations distribution in the whole volume of the oxygen electrode is homogenous and Sr migration to the electrolyte is not detected. Observed strict grouping of elements between layers shows good stability of the oxygen electrode material and its interface with GDC barrier layer.



Figure 77. EDS map of the Cell 7 oxygen electrode/GDC/electrolyte interface.



Figure 78. EDS scan of the Cell 7 cross-section after long-term degradation test.

The results shows stable distribution of the Sr across the air electrode (**Figure 78**). The Sr migration that was detected previously in the cells operated with steam as ASG here is not observed and even arrangement of Sr is confirmed. Additionally, also chromium measurements differ since no Cr was found in the sample operated with nitrogen as ASG. The LSCF stability was confirmed by XRD analysis, where mostly standard oxygen electrode reflexes were found (**Figure 79**).



Figure 79. XRD analysis of cell 7 after 1000 h test and reference pristine cell with LSCF electrode.

Additionally to confirm no issues related to the electrolyte and fuel electrode the EDS analysis for was performed on fuel side. The selected results are presented in **Figure 80**. The map of Ni, Y and Zr distribution in the fuel electrode functional layer shows homogenous arrangement of Ni and Zr elements with no agglomeration or migration.



Figure 80. EDS map of interphase of electrolyte and fuel electrode functional layer.

4.2.5. Discussion

The performed electrochemical and microstructural measurements allowed to verify the durability of the SOC cell operated in the electrolysis mode with nitrogen used as a sweep gas. The comparison of the current-voltage characteristics measured for different sweep gases (**Figure 68**) once again demonstrated the sufficient differences between typically used air and nitrogen. In the low range of current densities the differences were mainly driven by the OCV diversity. Nitrogen operation is showing much lower voltages than standard air. However, at the higher operating currents the nitrogen driven cells showed comparable curve development and finally at current densities > 1 A/cm² have identical progression to the air flushed samples and is able to reach high performance. This is expected results, since the oxygen content in nitrogen is increasing with operating current and at high oxygen flux the mixture is approaching air composition.

The long-term degradation experiment showed voltage evolution in the typical pattern of the standard operation of the electrolysis cell with the LSCF anode. Proper operation of the cell and good stability of the performance in 100% nitrogen atmosphere allowed comparison the results to the previously gathered data of LSCF failure in high steam concentration under the anodic operation. The variation of the voltage evolution during long-term experiments with steam an nitrogen are presented in **Figure 81**.



Figure 81. Comparison of the voltage evolution during long-term degradation measurements

The performance differences observed during in 1,000 h measurements showed that samples fed with nitrogen exhibit much lower degradation rate (\sim 1.2 %/kh) then found during operation with steam at the oxygen electrode (34 %/kh and 36 %/kh for the Cell 2 and the Cell 5 and even higher in other shorter examined samples).

The impedance spectra analysis allowed to identify the contribution of ohmic and polarization resistance in order to compare its progression during degradation tests (**Figure 82**)



Figure 82. Comparison of the Ohmic resistance and cell polarization change during long-term measurement of the Cell 5 and the Cell 7; Current density -0.25 A/cm². CFG: 70 vol. % H₂O / 30 vol. % H₂; ASG: 100 vol. % H₂O and 100 vol. % N₂, respectively.

When nitrogen was used as ASG the ohmic and polarization resistance rise only 21 m Ω cm² and 27 m Ω cm², respectively. These values are order of magnitude lower than found for the Cell 5 where much more severe growth of 464 m Ω cm² and 417 m Ω cm² was observed. Additionally, steam provoked a logarithmic-like pattern with almost two folds initial rise in r_p while for nitrogen operated cell only mild linear growth was registered.

Similar findings are present in the analysis of the distribution of the relaxation times. Where for steam as ASG some complicated mechanism was revealed (discussed previously) but DRT calculated for long term test with nitrogen as ASG showed minor degradation noticed only with P1 and some small redistribution of the intensity in the triad (P2-P4).

The reference and long-term DRT results also implies that there is some relation of peak P6 to the sweep gases with low oxygen content. The P6 is prominent only when pure steam or nitrogen were applied. Low oxygen partial pressure might influence the oxygen diffusion in LSCF material by suppressing the oxygen vacancies [159, 160]. At 800 °C the oxygen non-stoichiometry for H₂O or N₂ (expected oxygen partial pressure of $3-5 \times 10^{-6}$ atm) can approach oxygen vacancies of 0.2 per formula unit [161] hance limiting the oxygen migration. While steam decomposition of the LSCF perovskite structure led to a complicated development of peak P6 found in the Cell 5, for the Cell 7 operated with nitrogen, P6 after some initial stabilization remained stable for the whole degradation test.

Post mortem results comparison

Collection of SEM images of the microstructural morphology of cells operated for 1,000 h in various sweep gases is presented in **Figure 83**. The cross-section of pristine cell is used as a reference in order to compare obtained results. As was previously discussed the Cell 2 and Cell 5 clearly underwent some structural shift with severe morphological change distinguishable as a new interlayer visible as a dense region between oxygen electrode and GDC buffer layer. However, the Cell 6 (operated with nitrogen) shows no obvious defects or changes in morphology, what confirms the limited degradation found in electrochemical measurements.



Figure 83. Comparison of the microstructure of cells after long-term degradation tests and pristine sample.

Similar findings were registered for the EDS measurements. The comparison of the results between long-term operated Cells 2, 5 and 6 is presented in **Figure 84**. The Sr distribution in oxygen electrode for samples 2 and 5 exhibited harsh distortion. The area near the barrier layer are enriched with Sr content. In case for the Cell 6 operated with nitrogen as ASG no densification or element enrichment took place. The elemental composition of individual layers was not influenced by log-term degradation test. The visible differences in the cells morphology are in line with the electrochemical results.



Figure 84. The EDS maps comparison. Interface of oxygen electrode/GDC/electrolyte for cells 2, 5, and 6.

The strong performance degradation that took place during operation with steam as ASG is linked with morphological changes due to the LSCF material instability in steam. However, none of this alarming changes were found in cells swept by nitrogen (**Figure 85**). The XRD analysis revealed harsh differences in the results obtained for sample 5 and 7.



Figure 85. XRD analysis comparison of cell 5,7 and reference.

This findings confirm that low oxygen concentration in the sweep gas had limited effect on the degradation processes. However, the use of nitrogen as ASG has no added value in terms of system optimisation or operating cost reduction since there is no possibility to easily recover pure oxygen from the anode side.

4.3. Operation of the SOC cell under electrolysis mode with oxygen as a sweep gas

4.3.1. Objectives

The high degradation rate of the oxygen electrode found during operation of SOC with steam as ASG can limit the prospects of system integration of the concept. However, simultaneous production of pure hydrogen and oxygen in one device can still be achieved if the oxygen recirculation will be considered. Oxygen delivery to the anodic compartment is a viable option. In this chapter the performance of SOC operated with oxygen used as a anode sweep gas is presented.

4.3.2. Cell performance during long-term operation with oxygen as ASG

The performance of the SOC with oxygen used as a sweep gas was measured for 1048 h, in order to compare the results with data gathered for steam and nitrogen. The experiment was done for the Cell Type B. The long-term operation was done in electrolysis mode under constant current of -4 A. The cathode gas composition constituted 70% steam and 30% hydrogen. On the side of oxygen electrode only oxygen was supplied. **Table 16** presents the test characteristic parameters.

Fable 16. Op	erating conditions u	sed for l	long term	degradation	test with o	oxygen as a	ı sweep ş	gas
		a						

Tert	Duration	Cell	Current load	Anode		nt Anode		Cathode	e
I est Ino.	[h]		[A]	Flow [mNl/min]	Comp. [vol. %]	Flow [mNl/min]	Comp. [vol. %]		
Cell 8	1,048 h	Type B	-4 A	500 O ₂	100 O ₂	$90 \; H_2 + 210 \; H_2O$	70 H ₂ O		

The cell voltage behavior in the long run was monitored with intermittent EIS measurements. The voltage evolution under constant current is presented in **Figure 86**. During the test the cell presented a linear performance drop along the 1000 h operation. Starting voltage was 1022 mV and it evolved to 1199 mV at 1048 h of the measurement. The voltage shift amounted 177 mV.



Figure 86. Voltage evolution during long-term measurement of Cell 8; Current density -0.25 A/cm^2 . Flow composition C: 70 vol. % H₂O/ 30 vol. % H₂; A:100% O₂

The results shows a strong performance change for the cell operated with pure oxygen as a anodic sweep gas. The high voltage increase during long term experiment implies significant development of the cell resistance. The degradation rate was substantial and reached 168 mV/kh what corresponds to 16.5 %/kh. **Table 17** shows overall voltage changes for the Cell 8 during the whole duration of the test.

Table 17. The maximum voltage and overall degradation rate observed for cell 8 during the electrolysis operation with oxygen as ASG.

Test	Max Voltage	Overall degradation		
number mV		mV/kh	%/kh	
Cell 8	1,199 @ 1,048 h	168	16.5	

4.3.3. General electrochemical analysis of the Cell 8.

Analysis of sweep gas oxygen content depletion on polarization curves

Before the degradation test the influence of increasing the oxygen content in the ASG from air to pure oxygen in electrolysis mode is presented in **Figure 87**. The CFG was kept constant at 300 Nml/min and fixed gas composition 30 vol. % H₂ and 70 vol. % H₂O. The anode flow was

set to 500 Nml/min and different oxygen and nitrogen mixtures were used in order to investigate the cell behaviour.



Figure 87. Polarization curves of the Cell 8, operated in electrolysis mode under various oxygen concentrations in ASG.

The performance of the cell is somehow changed under varying sweep gas composition. However, the impact is not strong and the general shape and slope of the polarization curves remain very similar. The higher oxygen content in ASG causes a shift in voltage value, but it constitutes only 3% performance loss between air and pure oxygen, measured at -1 A/cm^2 . Additionally the impedance spectroscopy measurements were performed for different oxygen content in sweep gas in order to obtain more data concerning the cell the resistance. The obtained results are presented in form of Nyquist plot in **Figure 88** (left). The spectroscopy data were used in equivalent circuit model to match the values and unravel the resistance contribution **Figure 88** (right).

The results confirmed that the increase of oxygen content in air and even pure oxygen use do not have significant impact on the overall cell performance at least in short term measurements. The cell ohmic resistance rise from $170 \text{ m}\Omega \text{ cm}^2$ for air to $177 \text{ m}\Omega \text{ cm}^2$ for pure oxygen used as ASG. However, the cell polarization has decreased slightly with rising oxygen concentration from $112 \text{ m}\Omega \text{ cm}^2$ to $103 \text{ m}\Omega \text{ cm}^2$.



Figure 88. Measurement results for cell 8 of the influence of the oxygen content in the ASG. Impedance spectra analysis (left) and Cell resistances change (right)

Impedance spectra measurements during long-term operation

Systematically measured impedance spectra at several stages of the experiment allowed further analysis of the cell resistance and individual resistances contributions during the degradation test. The impedance spectroscopy results and data fit to the equivalent circuit model is presented in form of Nyquist graph in **Figure 89**. The progress of the spectra shows that the arc positions and semi-circles shape is significantly evolving during the test. The model fit allowed to identify the contribution of polarization and ohmic resistances. These contribution change during the long-term cell run are shown in **Figure 90**.



Figure 89. Evolution of impedance spectra during long-term measurement for the Cell 8; Current density -0.25 A/cm^2 . Flow composition cathode: 70 vol. % H₂O / 30 vol. % H₂; anode: 100 vol. % O₂

Both of the cell resistances grows along with time. The polarization of the cell changes from $98 \text{ m}\Omega \text{ cm}^2$ to $372 \text{ m}\Omega \text{ cm}^2$. The ohmic resistance at the start of the test was $181 \text{ m}\Omega \text{ cm}^2$ after 1000 h cell operation the value reached 660 m $\Omega \text{ cm}^2$.



Figure 90. Ohmic resistance and cell polarization change during long-term measurement for Cell 8; Current density -0.25A/cm². Flow composition C: 70 vol. % H₂O/ 30 vol. % H₂; A:100 vol. % O₂

The impedance spectroscopy data were used also for calculation of the DRT spectra. Analysis revealed five independent peaks. The long-term operation with oxygen as the sweep gas caused evident changes in the peaks character and contribution. Peaks 1-3 demonstrated growth while the peak 5 decreased gradually. The DRT spectra for degradation test with oxygen as ASG are presented in **Figure 91**.



Figure 91. DRT analysis long-term measurement of Cell 8; Current density -0.25A/cm². Flow composition cathode: 70 vol. % H_2O / 30 vol. % H_2 ; anode: 100 vol. % O_2

The strong evolution of the impedance and DRT spectra corresponds with the performance loss observed as rising voltage of the cell operated with pure oxygen as sweep gas.

Performance comparison before and after the long-term of degradation measurements

The evolution of the spectra allowed to observe the degradation during the test. Additionally to compare the performance of the cell, before and after degradation test, the I-V curves were registered. The comparison of the cell characteristics is presented in **Figure 92**. Severe shift of the characteristic line is noticeable. The cell before degradation test operated at -0.4 A/cm² need 429 mW/cm², but after long term operation at the same operating point power density increased to 547 mW/cm². This constitute a 27.5 % power demand raise.



Figure 92. Comparison of the polarization curves of the investigated cell 8 operated in electrolysis mode, measured before and after long-term degradation test. ASG: oxygen

Based on the polarization data the ASR was calculated from the linear part of the curves according to the equation 2.24 (Chapter 2.3.2). The ASR results were compared with the ones obtained from the impedance spectroscopy measurements and are presented in **Table 18**. The calculated values from both methods are very similar.

Table 18. Comparison of the ASR calculation results before and after long-term degradation measurements with nitrogen as a sweep gas for the Cell 8.

Sweep gas on the anode side	Measurement before or after long-term degradation test with steam	ASR calculated from linear part of polarization curve [Ω cm ²]	ASR calculated from impedance spectra [Ω cm ²]
Oxygen	before	0.284	0.279
	after	1.03	1.032

The degradation rate expressed in resistance is at the level of 711-718 m Ω cm²/kh.

4.3.4. *Post mortem* microstructural analysis sample cell 8

The microstructure of cell tested in the electrolysis mode with pure oxygen flow at the air side is presented in the Figure 93. Similarly to the cells operated with inert nitrogen no severe microstructural changes have been found during SEM analysis. However, some delamination at air electrode/barrier layer interface was detected in several areas. Additionally cracks were identified also near the LSCF surface, however its formation is attributed to disassembling process of the cell from the test housing **Figure 93** (bottom right). Still some of the similar cracks sometimes may be also found in the pristine cells.



Figure 93. Cross-section of the cell tested with O_2 as sweep gas: Full cell (top left); zoom at the interphase of air electrode/GDC/electrolyte/fuel electrode (top right); partial delamination of the LSCF layer from the barrier GDC (bottom left and top right), LSCF cracks at the electrode surface (bottom right)

In the next step of the *post mortem* analysis the EDS mapping and line scanning were performed in order to identify the element distribution and identify potential material changes. Figure 94 shows the EDS map of the cross section of interphase electrolyte/GDC layer/air electrode. The clear and smooth lines of individual layers in the cell are visible. Additionally cation distribution is and homogenous within the respective regions. Also, no cation migration has been identified in the analyzed sample.



Figure 94. EDS map of the cell 8. Elemental analysis of the interphase of air electrode – GDC – electrolyte.

Similar findings were registered by EDS line scan (Figure 95) where results confirmed that the elemental composition of each layer is maintained.



Figure 95. EDS line scan of the cell 8 cross-section after long-term degradation test.

4.3.5. Discussion

The measurements of the cell operated in electrolysis mode with oxygen as sweep gas allowed to verify the performance and stability of the SOC in the dedicated conditions. Short-term characteristics of the cell under rising oxygen concentration in the sweep gas revealed that replacement of air by pure oxygen has only minor impact on the cell performance in short runs. The cell voltage is slightly shifted, however, the overall cell power is changed only by 3% (performance drop in comparison to air as ASG). This effect is expected and similar observations were measured in the work [150]. The spectroscopic analysis showed that in short run the performance drop in comparison to the standard conditions is related only to the ohmic resistance since the cell polarization decreased slightly with rising oxygen concentration.

In the long degradation test the cell operated with oxygen as ASG presented a linear-like voltage rise under moderate current densities. The degradation rate calculated based on the voltage

change amounted 16.5 %/kh. This behaviour implies clearly that some degradation processes took place in the cell when operated with pure oxygen. To unravel the origin of high degradation further data analysis from sspectroscopy measurements was performed. It revealed that both the polarization resistance and ohmic resistance was developing during the test, however the overall resistance change was mainly related to the ohmic resistance. DRT calculation showed that the group of peaks from P1 to P3 is responsible for resistance increase. Such resistance development is usually related to some delamination processes [162]. The decrease of the peak P5 can also be attributed to the delamination due to the enhanced diffusion transport in the electrode caused by cracks and delamination development. Microstructural microscope observation confirmed the delamination of the layers at the oxygen electrode region. Additionally, the elemental analysis turned down the possibility of cell material deterioration. Obtained results indicate that the operation of LSCF oxygen electrode in pure oxygen leads to cell performance degradation by gradual delamination of the electrode. The process might be similar to the one observed with LSM electrode when due to poor oxygen ion conductivity the oxygen build up near the OE led electrode detachment from electrolyte [105]. Here high oxygen concentration at the anode side may cripple the oxygen transport and causes the oxygen pressure build up similar to the one observed with LSM.

5. General discussion

Investigation of the LSCF-based electrode stability during operation in the electrolysis mode was focused around possibility to produce hydrogen and recover pure oxygen from the electrolyzer cell. For this purpose the solid oxide cell samples were supplied with steam or oxygen on the oxygen electrode side. This two gases offers a possibility of easy recovery of oxygen either by steam condensation or oxygen recirculation. Goal was to the operate cells in long term tests in order to gather value electrochemical data for study of the degradation effect related to the use of the mentioned sweep gases. After the long-term electrochemical measurements the influence of the extreme humidity and high oxygen content on the LSCF electrode material microstructure and stability was also investigated in the *post-mortem* analysis.

Table 19 presents a comparison of overall degradation obtained during long-term tests of presented SOE cells. In all of the test with steam as ASG the voltage increase was significant. However, the highest values of degradation rate were registered for Cells 1, 3 and 4, for which the overall degradation reached values higher than 43%/kh. In case of degradation of samples 2 and 5 obtained values were at similar level and did not cross 36%/kh.

Test	Duration	Cell	ASG	Max Voltage	Overall de	egradation
number	[h]			mV	mV/kh	%/kh
Cell 1	>200 h	Type A	H ₂ O	1,051 @ 200 h	890	102
Cell 2	1,000 h	Type A	H ₂ O	1,299 @ 1,000 h	344	36
Cell 3	>600 h	Type B	H_2O	1,300 @ 600 h	447	43
Cell 4	>300 h	Type B	H ₂ O	1,282 @ 350 h	637	60
Cell 5	1,000 h	Type B	H ₂ O	1,301 @ 1,000 h	329	34
Cell 6	1,061 h	Type A	N_2	935 @ 1,061 h	11.3	1.22
Cell 7	1,000 h	Type B	N_2	911 @ 1,000 h	11	1.20
Cell 8	1,048 h	Type B	O ₂	1,199 @ 1,048 h	168	16.5

Table 19. Comparison of the degradation test results for cells operated in electrolysis mode with various ASG.

The high differences are corelated with the duration of the test. The shorter tests showed higher degradation however this might be related to the degradation characteristic which was shown to be higher in early stage of the operation. When only the initial degradation rate is taken into account (up to 200 h) the values change in similar pace (**Table 5** and **Table 6**).

The reference measurements (Cell 6 and Cell 7) were conducted to investigate the possible degradation effects related to low oxygen content in the sweep gas. For this purpose the nitrogen

was used as ASG in order to keep similar low oxygen partial pressure on the oxygen electrode. The long degradation runs reveled that the overall degradation rate for this reference test leveled around 1.2 %/kh what is order of magnitude lower than found for samples tested in steam and oxygen. This results suggests severe impact of steam and oxygen on the LSCF cell performance.

However, further electrochemical analysis was conducted for the Cells 5, 7 and 8 in order to revel the origin of the performance loss. **Figure 96** presents the voltage evolution for each selected sample during 1000 h of operation in electrolysis with various sweep gases. The character of the changes is visibly different for each individual case.

The reference sample swept with nitrogen showed only minimal voltage change. In the later cases the voltage rise is substantial, but the appearance of the changes differ. The cell swept with oxygen demonstrated a linear growth throughout the whole duration of the experiment. The cell that was swept with steam demonstrated a logarithmic type growth in the early stage of the test (< 200 h) and then the behavior changed its character to a linear progression. This differences suggests different origins of the degradation processes.



Figure 96. Comparison of voltage evolution during long-term measurement for various anode sweep gas (cell 5, 7 and 8); Current density -0.25 A/cm². Flow composition C: 70 vol. % H_2O / 30 vol. % H_2

The further search of the degradation source for each sweep gas was conducted based on the data from impedance spectra and galvanostatic measurement obtained before and after each long-term test. This measurements allowed to anticipate the resistance of the cells with two independent methods. The comparison of the obtained results is presented in **Table 20**.

Test number	ASG	Measurement before or after long- term degradation test	ASR calculated from linear part of polarization curve	ASR calculated from impedance spectra	Resistance degradation from galvanostatic measurements	Resistance degradation from EIS measurements
			$[\Omega \text{ cm}^2]$	$[\Omega \text{ cm}^2]$	$[\Omega \text{ cm}^2/\text{kh}]$	$[\Omega \text{ cm}^2/\text{kh}]$
Cell 5	H ₂ O	before	0.416	0.437	0.898	0.881
		after	1.314	1.318		
Cell 7	N_2	before	0.313	0.329	0.068	0.049
		after	0.381	0.378	_	
Cell 8	O_2	before	0.284	0.279	0.712	0.719
		after	1.03	1.032	-	

Table 20. Comparison of the ASR calculation results before and after long-term degradation test for selected cells.

The ASR calculation based on two independent data sets and analytic methods have a good correlation and results obtained from two different measurements show similar values. Both methods revealed a severe resistance degradation when oxygen and steam were used as ASG what explains the reason of such intensive voltage increase during the tests. The resistance degradation reached 0.712-0.719 Ω cm²/kh and 0.881-0.898 Ω cm²/kh, respectively. However, the cell operated with nitrogen as ASG showed only 0.049-0.068 Ω cm²/kh resistance degradation what is in line with previously discussed voltage evolution results and confirms much lower influence of the nitrogen on the stability of the cell in comparison to oxygen and steam. The deeper analysis of the EIS spectra allowed to distinguish contributions to the resistance and its values along the degradation measurements for various sweep gases (Figure 97).



Figure 97. Comparison of ohmic resistance and cell polarization change during long-term measurement for various anode sweep gas; Current density -0.25 A/cm². Flow composition C: 70 vol. % H₂O/ 30 vol. % H₂

The ohmic resistance is evolving in a linear manner in all of the cases. For the reference test (Cell 7) there is only minor rise of the ohmic resistance $(21 \text{ m}\Omega \text{ cm}^2)$. The rate of change in case of the Cell 5 (steam) and the Cell 8 (oxygen) is at the similar level and ohmic resistance is rising gradually along 1000 h-long tests. The linear change of the ohmic resistance is usually associated with delamination processes or crack formation and is probable cause for some of the performance loss in both discussed alternative sweep gases. Additionally, the polarization resistance for each ASG provokes different cell response in the long-term run. For steam, a logarithmic-like pattern was found. In this case the profile change is sufficiently different from the results obtained for oxygen sweep gas what suggest different origin of the degradation. In case of reference cell the resistance behavior fits the pattern of the normal operation of the electrolysis cell with the LSCF anode.

Similar founding's were confirmed by the DRT analysis. For all of the cases six apparent peaks related to various processes were identified. In the reference test with nitrogen as ASG only some small changes with peak P1 and some mild redistribution of the intensity in the triad (P2-P4) was noted what is in line with other previously analyzed results reporting typical degradation rate for electrolysis cell.
As was expected, more complicated peak development were found when steam was used as sweeping gas in anode compartment. The detailed analysis of DRT spectra for this scenario was previously discussed in 4.1.5.1. The most interesting changes took place during initial 300 h with intriguing development of P1 and P2. At this frequency range (10-90 kHz) typical processes are related to charge and oxide ion transfer in the mixed ionic-electronic oxygen electrode. The LSCF decomposition (with creation of many secondary phases) that was later confirmed by the *post-mortem* analysis most probably led to weakening of the charge and ionic conductivity causing the rapid resistance increase.

In case of the Cell 8 the DRT calculation revealed gradual change (rise) in peaks from P1 to P3 and decrease of the peak P5 what is connected with delamination processes. The electrochemical measurements with the long-term observation allowed to question the hypothesis of sufficient stability of LSCF material in both alternative sweep gases: steam and oxygen.

The *post-mortem* investigations conducted with each of the tested samples allowed to also reject hypothesis of possible stable operation in electrolysis mode in extreme humidity or pure oxygen on LSCF material. The microstructural investigations showed that in case of steam the creation of many secondary phases and fatal de-mixing of the LSCF layer is responsible for extreme degradation rate of the cell. The SEM images allowed to discover a secondary Sr based layer created due to the LSCF decomposition in steam. For oxygen operated cell the main reason of poor stability was layer delamination probably caused by oxygen build up. The comparison of the cross section of the cells after testing is presented in **Figure 98**. The detailed analysis of the microstructures were discussed previously.



Figure 98. Comparison of the microstructure of SOC cells operated with various sweep gases in long-term degradation tests.

6. Conclusions

This work focuses on degradation of the LSCF-based oxygen electrode in solid oxide cells operated in the electrolysis mode. The idea was to carry out a long-term degradation tests with alternative sweep gases that offer additional advantage - possibility of production of high quality oxygen together with hydrogen in one electrochemical device. The main goal was to evaluate the degradation effects related to the use of promising sweep gases and anodic polarization of the solid oxide cell. During the investigation, the eight long-term durability tests have been conducted , allowing to perform insight electrochemical characterization of the cells. Moreover, in order to understand the cause of the cells performance drop, the post-mortem analysis was performed for all of the tested samples that outlined the microstructural and material changes. Both proposed investigation paths reveled poor stability of the LSCF material in proposed, challenging conditions.

- The electrochemical analysis for cells operated with steam as ASG indicated that the oxygen electrode did not present sufficient stability in the 1000 h experiment. Rapid performance loss with complicated evolution of the electrochemical processes in conjunction with gradual ohmic resistance increase was identified. <u>Primary hypothesis</u> <u>disproved</u>
- Microstructural analysis found that the source of the problems was de-mixing of the cations in LSCF material followed by the formation of a Sr-enriched region near the barrier layer that was prone to chromia capture.
- The tests with nitrogen used as a ASG, allowed to obtain the reference data and disprove supposition of significant impact on degradation, related to low oxygen content in the sweep gas
- The poor stability of the cell was also discovered when cell was swept with pure oxygen. Here the performance loss was at similar level as was found for steam usage as ASG. However the behavior of the cell fitted more to the pattern that is connected with delamination-based degradation what was later confirmed by microscope imagining. <u>Secondary hypothesis disproved</u>

The presented work shown that while separation of pure oxygen in high-temperature steam electrolysis is possible with LSCF anode, the sustaining of the initial performance of the electrolysis cell is challenging and requires additional studies. It is clear that usage of steam or oxygen as the anode sweep gas is an attractive area of interest, especially when application in

real industrial system is considered. Simultaneous hydrogen and oxygen production offers some interesting gains and advantages particularly when steam is already available onsite. However, as was proven in this thesis the direct usage of state-of-the-art materials may not be possible and additional research focus on dedicated anode layers may be required to reach acceptable performance.

- The future of this concept lay more in material science field where new electrodes need to be elaborated. The properties of these materials have to presents high oxygen mobility and stability when used with pure oxygen to avoid delamination.
- In case of operation with high steam content the developed materials should offer good stability against cations de-mixing in extreme humid atmospheres. Some of this properties may be looked for among alkaline-earth-free perovskites or Ruddlesden– Popper phases.

Additionally, some operational techniques might be further investigated, such as temperature decrease, or specific management of the gas flows.

- The reduction of the operating temperature might improve material stability by thermodynamically and kinetically limiting the Sr segregation and may also inhibit Cr poisoning, however it will inevitably reduce the LSCF conductivity of oxygen ions influencing the overall cell performance. The direction of lowering operating temperature is in line with the current trends in SOC technology development, since it leads to lowering OPEX cost during cell fabrication and CAPEX costs associated with use of high temperature resistant steel and dedicated alloys in the hydrogen systems.
- For pure oxygen operated cells, a high oxygen recirculation might be attempted in order to change the character of sweep gas flow. This may have some positive impact on oxygen removal from electrode pores an in consequence limit the oxygen build-up and LSCF delamination.

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