Sector coupling using SOECs via co-electrolysis of CO2 and H2O

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Publication date: 2019

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Sector coupling using SOECs via co-electrolysis of $\text{CO}_2$ and $\text{H}_2\text{O}$

Megha Rao

Risø 2019
Summary

The shift to renewable energy sources for power production in order to decrease the CO$_2$ emissions has led to rise in the demand for research in the field of energy storage technologies. One of the interesting options for storing excess renewable energy obtained from sources such as solar and wind is via the production of hydrocarbons. Utilization of solid oxide electrolysis cells (SOECs) facilitates this technology, known as Power-to-Liquid (PtL) and Power-to-Gas (PtG). This thesis is titled Sector coupling using SOECs, since integration of renewable energy production and storage to meet the grid demands can be approached with the use of SOECs for chemical production. However, the commercialization of SOECs is accompanied by the challenge of degradation under long-term operation. This PhD thesis focuses on the production of syngas, which is a valuable precursor for downstream production of fuels such as methane, using co-electrolysis wherein excess renewable energy can be stored. The aim of this work is to form methane internally at high pressure conditions, for which SOEC process model has been designed in Chapter 7. The novelty also lies in the use of wind profile from the Danish island of Bornholm for running cell and stack for dynamic energy storage.

State-of-the-art (SoA) cells consisting of a nickel-yttria stabilized zirconia (Ni-YSZ) fuel electrode, YSZ electrolyte and lanthanum strontium cobaltite ferrite-gadolinium doped ceria (LSCF-CGO) composite oxygen electrode, were initially tested under co-electrolysis (H$_2$O+CO$_2$) conditions. A comparison between galvanostatic and potentiostatic modes was performed. For the purpose of degradation analysis, electrochemical impedance spectroscopy (EIS) was used along with microstructural analysis. Area specific resistance (ASR) was used as an indicator for comparing the extent of degradation. Potentiostatic mode of operation helped protect the cell by lowering the current density during long-term operation thereby keeping the overpotential over the cell constant.

Following this, improvement in the cell structure was suggested in the form of modification of electrode microstructure. For the oxygen electrode modification, infiltration of solution was performed on a porous backbone layer. The solution consisted of lanthanum strontium cobaltite (LSC) which was infiltrated on CGO backbone. For the fuel electrode modification, change in the particle size and density of the Ni-YSZ was performed.

The improved cell was further tested under dynamic load cycling conditions as a candidate for energy storage in the form of methane. However, this is a very challenging task which requires the optimization of electrodes, test protocols etc. obtained as a result of ambient pressure tests carried out in Chapter 2 and 3. Co-electrolysis...
operation was performed on cell and stack level for 1000 hours. In the context of co-electrolysis operation, the presence of leaks was investigated in detail. Electrochemical and microstructural analysis of the electrodes and electrolytes helped in the formation of the theory of diffusion of H\textsubscript{2} and O\textsubscript{2} through the pinholes along with flow dependency.

The improved cell was also tested under pressurized conditions up to 10 bar. The high pressure test was performed by applying steam electrolysis. Impedance data modeling was performed to draw a correlation between pressure and the electrode performance.

Ultimately, the long-term goal will be to enable direct methane production via high pressure SOEC operation. In this perspective, process modeling was performed, using the data from the experimental analysis to validate the model.


Efter dette blev forbedring i cellestrukturerne antydet i form af modifikation af elektrodemikrostruktur. Til iltelektrodemodificeringen blev en infiltration med en katalytisk opløsning udført på et porøst rygradlag. Opløsningen bestod af lanthanum strontium cobaltit (LSC), som blev infiltreret på CGO-rygraden. Til brændstofelektrodemodificeringen blev der udført ændringer i partikelstørrelsen og densiteten af Ni-YSZ.

I sammenhæng med co-elektrolysedrift blev tilstedeværelsen af lækager omhyggeligt undersøgt. Elektrokemisk og mikrostrukturerel analyse af elektroder og elektrolytter hjalp med til dannelsen af diffusionsteorien af $H_2$ og $O_2$ gennem pinhullerne sammen med flowafhængigheden. 

Den forbedrede celle blev også testet under tryk op til 10 bar. Højtryktesten blev udført under dampelektrolyseforhold. Impedansdatamodellering blev udført for at tegne en sammenhæng mellem trykket og elektrodens ydelse. 

I sidste ende vil det langsigtede mål være at muliggøre direkte metanproduktion via SOEC-drift med højt tryk. I dette perspektiv blev processmodellering udført ved hjælp af dataene fra den eksperimentelle analyse til valideringen af modellen.
Preface

This thesis is submitted in candidacy for the Ph.D. degree from the Technical University of Denmark (DTU). The work was carried out at the Department of Energy Conversion and Storage in the period from August 2016 to August 2019 with three months of research activities at École polytechnique fédérale de Lausanne (EPFL), Sion, Switzerland. The project was supervised by Anke Hagen, Dr. Prof., and co-supervised by Xiufu Sun, Dr., Søren Højgaard Jensen, Prof., Dr. and Peter Vang Hendriksen, Prof., Dr. This work was funded by European Union’s Horizon 2020 framework program (H2020) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement no. 699892 (“Efficient Co-Electrolyser for Efficient Renewable Energy Storage-ECo”). This thesis is a collection of papers appended at the end as accepted and/or submitted and under review.

Risø, November 18, 2019

Megha Rao
Acknowledgements

I would firstly like to thank the Technical University of Denmark for providing me with the opportunity to carry out my PhD project.

I would like to thank my supervisor Anke Hagen for supporting me with my PhD thesis.

My heartfelt appreciation goes to my co-supervisors Xiufu Sun and Søren Højgaard Jensen for always motivating and guiding me in the right direction throughout my PhD. I would also like to thank Mogens Bjerg Mogensen and Anne Hauch for supporting me scientifically and emotionally during the last year of my PhD. A special thanks to Rasmus Bjørk and Lars Nilausen Cleeman for guiding me in the last year. I would also like to thank Heidi and Aniita for all the administrative help during my PhD.

Needless to say, an experimental PhD cannot be finished in time without the help of amazing technicians. I would like to thank Henrik Henriksen, Mahbooba Davodi, Jens Østergård, Bent Forster Hansen and Ole Hansen. Additionally, I would like to thank Søren Koch for helping me with the smooth progress of experiments and Karl Thyden for guiding me with the microscope at all times. The experiments would not have been possible without the excellent cells prepared by Karen Brodersen and Lene Knudsen.

I would like to take this opportunity to thank Jan Van Herle at EPFL, for hosting me and motivating me to think outside the box during my exchange, along with ski lessons. I would not have enjoyed Switzerland without Guillaume, Giorgio, Ligang, Gauthier, Mar, Arata, Stefan, David, Chantal and last but definitely not the least Hugh. In this regard, I would like to acknowledge the support of Otto Mønsteds foundation for funding my exchange as well as supporting a conference participation. To complete this PhD, I had the utmost support of my family, especially my parents.

A special thanks to my sister Manisha Rao for being a constant supporter of my dreams and for being the smart woman who inspired me everyday. I would like to thank my uncle for being the sensible adult I could talk to whenever I needed.

Risø is a special place to work at and so are the wonderful friends I made during these 3 years, who stood by me in thick and thin to make sure that I finish my PhD on time. I would like to sincerely thank Simon (the one I can rely on), Nedo (the ever smiling angel), Ilaria, Steven, Grichar, Oscar, Vanessa (the foodie), Hendrik, Kabitri, Fabrizio, Peyman, Xu, Maria, Daniel, Jyoti, Dordije, Kristina, Matti, Sini, Robert, Kaushik, Moumita, Eugene (my counsellor), Giovanni (both of them), Massimo (my go to person), Jan (the coolest German) and Rocio, Tuk, Elise, Kevin (the Aussie weirdo) and Peter. I would also like to thank my Danish
teacher, Annemette Skøt Hansen for always motivating me to learn Danish and keep up with my PhD. In addition, I would like to show my appreciation towards my wonderful physiotherapist Synnøve, who motivated me to never give up. Last but not the least, I would thank some special people, from the bottom of my heart, who made me feel at home. Linda Bang Jessen was literally my mother in the past 3 years, and I owe her everything. My best friend Teresa was the one I laughed and cried with during each passing day of my PhD and I can not thank her enough. I need to thank my big brother Tiago for teaching me life lessons and helping me get through my PhD. I would like to thank Dimitris (the witty one), Erika, Rafa, Digvijay, Metin, Rishi, Selene, Alvaro, Gautham, Kamakshi, Ajinkya, Sagar, Maitreyi, Nishant and Brendon for being there since my Delft days. I can not forget my crazy flatmates Anna (for being so kind and patient and for making me run), Anne, Jess and Gisken, who made it worthwhile in Copenhagen. Lastly, a big hug to Happy, Ajit, Anushruti, Anshul, Supreet, Janki, Rishi, Aasma, Ananya, Sohini, Ganesh and Binu for being there for me for past 9 years or more. It is worth mentioning that I derive my strength from watching Rafael Nadal for his fighting spirit and for still winning grand slams, along with Arsenal for always delivering good football for the fans. I would like to dedicate this PhD to my Grandma (the coolest one in my family).
Manuscripts included in this thesis

- **Paper I**: A Comparative Study of Durability of Solid Oxide Electrolysis Cells Tested for Co-Electrolysis under Galvanostatic and Potentiostatic Conditions
  
  **M. Rao**, X. Sun, and A. Hagen
  
  **My work**: Performing literature review and experiments, along with data analysis and interpretation; and writing of the first draft

- **Paper II**: Unwinding entangled degradation mechanisms in Solid Oxide Electrolysis Cells through electrode modifications and impedance analysis
  
  **M. Rao**, S.H. Jensen, X. Sun, and A. Hagen
  
  **My work**: Performing literature review and experiments, along with data analysis and interpretation; and writing of the first draft

- **Paper III**: Durability of Solid Oxide Electrolysis stack under dynamic load cycling for syngas production
  
  **M. Rao**, X. Sun, and A. Hagen
  
  **My work**: Performing literature review and experiments, along with data analysis and interpretation; and writing of the first draft

Manuscripts not included in this thesis

- **Proceeding I**: Long Term Testing of Solid Oxide Electrolysis Cells under Co-Electrolysis Conditions
  
  **M. Rao**, X. Sun, and A. Hagen
  
  **My work**: Performing literature review and experiments, along with data analysis and interpretation; and writing of the first draft

- **Proceeding II**: Durability of SOECs with modified electrodes
  
  **M. Rao**, X. Sun, and A. Hagen
  
  **My work**: Performing literature review and experiments, along with data analysis and interpretation; and writing of the first draft

- **Proceeding III**: Effect of Leaks in Solid Oxide Electrolysis Cells Tested for Durability under Co-Electrolysis Conditions
  
  **M. Rao**, S.H. Jensen, X. Sun, A. Hagen, and M.B. Mogensen
  
  **My work**: Performing literature review and experiments, along with data analysis and interpretation; and writing of the first draft
• **Paper IV:** Power-to-methane via co-electrolysis of H₂O and CO₂: The effects of pressurized operation and internal methanation
  Ligang Wang, Megha Rao, Stefan Diethelm, Tzu-En Lin, Hanfei Zhang, Anke Hagen, Francois Maréchal, Jan Van Herle
  **My work:** Performing SOEC electrochemical model validation with experimental data set along with contributing to the writing of the manuscript
Acronyms

AC Alternating Current
ASR area specific resistance
CEA Commissariat à l’énergie atomique et aux énergies alternatives
CONV gas conversion
DGM Dusty Gas Model
DIFF gas diffusion
DRT distributions of relaxation times
DTU Technical University of Denmark
R_p polarization resistance
R_s serial resistance
EC Electrolysis
EDX Energy-dispersive X-ray spectroscopy
EIS Electrochemical Impedance Spectroscopy
EPFL École polytechnique fédérale de Lausanne
EU-ECo Efficient Co-Electrolyser for Efficient Renewable Energy Storage-ECo
FC Fuel cell
FM Fick’s model
GDC gadolinium doped ceria
LSC (La, Sr)CoO_3
LSC-CGO (La, Sr)CoO_3-Gd:CeO_2
LSCF (La, Sr)(Co, Fe)O_3
LSCF-CGO (La, Sr)(Co, Fe)O_3-Gd:CeO_2
LSM (La, Sr)MnO_{3-δ}
LSM-YSZ (La, Sr)Mn_{3-δ}Y_2O_3:ZrO_2
MIEC mixed ionic electron conductor
Ni-YSZ Nickel-yttria stabilized zirconia
NmLPM Normal millilitre per minuter
OCV open circuit voltage
PID Proportional-integral-derivative
PtL Power-to-Liquid
PtG Power-to-Gas
SEM Scanning electron microscopy
SMM Stefan Maxwell Model
SMR Steam methane reforming
SoA State-of-the-art
SOEC Solid Oxide Electrolysis Cell
Acronyms

TPB triple phase boundary
WGS Water gas shift
YSZ yttria stabilized zirconia
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CHAPTER 1

Introduction

Widespread use of renewable energy sources for power production has gained significant attention, especially for the case of Europe. EU directives recommend the use of such technologies to lower the greenhouse gas emissions [1]. For the case of Denmark, in particular, 50% of electricity is already being produced through wind turbines with a goal of turning into a completely renewable based economy by 2050 [2]. Solar and wind have been reported to be the most matured form of renewable energy in use currently [3–5]. However, these sources produce intermittent energy which needs to be stored in order to balance the demand and supply chain [6]. In this regard, the most commonly used energy storage media consist of batteries, compressed air and flywheels [3–5]. An interesting aspect in this respect is the storage of energy in the form of chemicals which can be rendered useful as fuels. This is known as Power-to-Liquid (PtL)/ Power-to-Gas (PtG) conversion. To elaborate, fuels used in the transport sector can be directly connected to the grid with the help of SOECs, wherein excess renewable energy produced by wind turbines would be converted to fuels. This concept is known as sector coupling [7]. Furthermore, cross-vector coupling takes advantage of Power-to-X and helps cope with seasonal variations. It also aims at decarbonisation and a decrease in energy losses by optimizing the integration.

1.1 Energy storage in PtL/PtG scenario-Solid oxide electrolysis cells (SOECs)

In the transport sector, fuels with high calorific value such as methane can be integrated in the pre-existing infrastructure. This methane can be produced by the use of renewable energy technologies by reusing the emitted CO$_2$ [8]. For this purpose, high temperature electrolysis using Solid oxide electrolysis cells (SOECs) is of essence. Due to the high conversion efficiency (theoretically up to 100%) [9], SOECs can be operated for CO$_2$ conversion thereby utilizing the CO$_2$ emitted and decarbonizing the environment. There is a growing need of synergy between renewable energy and the transport sector [8], which can be facilitated by the use of SOECs in the future. Furthermore, SOECs have the advantage of converting CO$_2$ and steam simultaneously through a process known as co-electrolysis [3, 5, 10, 11]. These cells operate in the temperature range of 600-1000 °C. The working principle of SOEC is displayed in Figure 1.1. Here, excess wind energy is used to convert steam and CO$_2$ such that syngas is formed. A SOEC consists of a fuel electrode, an oxygen electrode and an
electrolyte. The reactions taking place are as follows:

\[
H_2O \rightarrow H_2 + \frac{1}{2}O_2 \quad (1.1)
\]

\[
CO_2 \rightarrow CO + \frac{1}{2}O_2 \quad (1.2)
\]

\[
CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (1.3)
\]

Figure 1.1: Working principle of SOECs [12].

On the fuel electrode, steam and \( CO_2 \) are fed. Oxygen evolution reaction takes place and only \( O^{2-} \) is transported through the electrolyte to the oxygen electrode. \( H_2 \) and CO are obtained at the fuel electrode. Thermodynamically, these reactions are endothermic in nature. In order for the reaction to proceed at 750 °C, excess energy in the form of heat from an external source needs to be provided. However, this heat can also be provided by the Joule heat generated in the cell during operation. Figure 1.2 shows the energy demand in terms of heat and electricity. At thermoneutral voltage, no excess energy needs to be provided for the reaction to proceed, making it desirable to run the cell under constant thermoneutral potential. This potential is determined by the reactions occurring at a certain temperature in thermodynamic equilibrium.
1.2 SOEC electrodes and their degradation

Operation of SOEC poses the challenge of short lifetimes. Cells with a lifetime of 5-10 years are desired and demonstration work is being performed on understanding the mechanisms related to the performance of cells and degradation with regard to the testing modes [14, 15]. A state-of-the-art (SoA) fuel electrode supported SOEC consists of a fuel electrode and support made out of nickel-yttria stabilized zirconia (Ni-YSZ) fuel electrode, a YSZ electrolyte, a cerium gadolinium oxide (CGO) barrier layer and an oxygen electrode. The oxygen electrode can be made up of Mixed Ionic electronic conductors such as lanthanum strontium cobaltite ferrite-cerium gadolinium oxide (LSCF-CGO) or lanthanum strontium cobaltite-cerium gadolinium oxide (LSC-CGO), or a lanthanum strontium strontium cobaltite-cerium gadolinium oxide (LSM-CGO) composite oxygen electrode. Degradation of the cell during testing has been reported for over 1000s of hours [16]. Degradation has been found in the fuel electrode due to coarsening of nickel in the active electrode, along with the migration of Ni particles from the active layer to the support, together with loss of active contact area for a triple phase boundary (TPB) reaction and loss of percolation [15, 17]. A TPB ionic conduction path is displayed in Figure 1.3.
Additionally, impurities in the gas stream may lead to loss of active area and cause microstructural damage [18, 19]. Degradation of the oxygen electrode due to resistance to the oxygen evolution reaction has been investigated previously [20, 21]. Furthermore, increase in the ohmic resistance due to high current densities also leads to irreversible degradation [14]. Moreover, leaks in the cell during testing might lead to generation of hot spots leading to increase in the resistance [22]. Microstructural analysis on a stack tested for over 10000 hours also reported a combination of the aforementioned degradation mechanisms [23]. These issues need to be addressed by modifying cell microstructure and operating parameters prior to commercialization of cells.

1.3 Thesis objective

This PhD is focused on the integration of SOECs in the methane production sector. It aims at connecting the end users with the suppliers. In this work, the conversion of CO$_2$ and steam to methane by using dynamic wind energy production is comprehensively discussed. Methane production is of essence owing to the availability of infrastructure as well as techno-economics of the SOEC-methane system, as reported earlier [24]. SOECs are of utmost importance, and the testing and characterization of SOECs is discussed in detail. System modeling in Power-to-methane context is also discussed to get an overview. The aim was to produce methane internally, especially under pressurized conditions [25]. The work performed at 1 bar experimentally is under co-electrolysis conditions aimed at methane formation with a fuel gas composition of 65% H$_2$O + 25% CO$_2$ + 10% H$_2$. for the case of pressurized testing, steam electrolysis characterization was performed. The outline of the thesis is as follows:
• Chapter 2 relates two testing modes, namely, galvanostatic and potentiostatic for the SoA cells to understand the impact of testing modes

• Chapter 3 serves to comprehensively understand the degradation mechanisms in cells with different electrode structures

• Chapter 4 demonstrates the use of SOECs under dynamic load cycling conditions and the impact on degradation

• Chapter 5 highlights the effect of leaks on the cell test data and guides the reader to understand the uncertainty and the origin of it

• Chapter 6 discusses the analysis of the results obtained under pressurized steam electrolysis up to 10 bar

• Chapter 7 describes the process model which validates the experimental data obtained in this work and helps to predict the optimized conditions for methanation

• Chapters 8 and 9 summarize the PhD work along with insights for the future work
Durability testing—comparison between galvanostatic and potentiostatic testing modes

2.1 Introduction

In the context of PtG/PtL methane production using SOECs, it is desired to operate the cell at thermoneutral voltage such that technically no excess energy needs to be provided or taken away from the cell [9, 10]. Traditionally, most of the cell tests on the lab scale have been carried out under galvanostatic conditions i.e., under constant current such that the cell voltage increases as the cell degrades. This testing mode has the advantage of the ease of instrumental control. Another mode of testing, where the voltage remains constant while the current density decreases as the cell degrades, is known as potentiostatic mode of operation. Thermoneutral operation can be performed by setting the cell voltage to thermoneutral voltage (e.g. 1.29V for steam electrolysis) [26]. This served as a starting point for this PhD thesis, wherein these two testing modes were compared, and the degradation analysis was carried out.

This chapter incorporates the results from Manuscript-1, as published. In this chapter, state-of-the-art (SoA) fuel electrode supported cells were tested for durability under co-electrolysis conditions. The cells were tested under galvanostatic and potentiostatic conditions and a comparison was drawn between the operational modes. The aim of attaining an operating lifetime of 5-10 years brings about the need for testing for thousands of hours to comprehensively understand the degradation mechanisms pertaining to various operating conditions.

Previous studies have shown that the degradation of SOECs is attributed to both fuel and oxygen electrode [19, 27], which was also observed during this PhD work [28, 29]. For the contribution from the fuel electrode, Ni migration and Ni coarsening, along with the effect of impurities have been previously reported [16, 17, 30, 31]. For the oxygen electrode, the delamination of the electrode from the electrolyte and the barrier layer has also been reported [20].

In case of galvanostatic testing, a TPB would be under increasing overpotential due to increasing voltage related to the degradation, which in turn will lead to the involvement of more TPB sites to achieve the same current density through ionic conduction. On the other hand, for potentiostatic testing as the cell degrades, the current density
experienced by a TPB decreases, thereby leading to lesser ionic conduction requirements since the current density decreases. A comprehensive discussion of operation of the state-of-the-art (SoA) cells under both modes of operation is described in this chapter.

2.2 Experimental

Fuel electrode supported SoA cells, with Nickel-Yttria Stabilized Zirconia (Ni-YSZ) fuel electrode with a thickness of 220-260 µm, a 6-10 µm thick YSZ electrolyte, a CGO inter-diffusion barrier layer and a 40-60 µm thick composite oxygen electrode of lanthanum strontium cobaltite ferrite-gadolinium doped ceria (LSCF-CGO), were tested in this work. The active area of the cells was 16 cm². The test setup has been previously described in literature [32, 33]. The cells were mounted in a test house made of alumina consisting of gold on the oxygen side and nickel on the fuel side as the current collector contact components, along with a gold sealing on the fuel side. During the start up, in order to ensure gas tight sealants and electrical contact between the cell and the contact components, a weight of 4 kg was applied. The cells were heated to 800 °C with a ramp rate of 60 °C per hour, and the cells were held for 2 hours prior to reduction. During the heating up of the cells, N₂ was supplied to the fuel electrode while air was supplied to the oxygen electrode. The cells were reduced with N₂ and H₂ beginning from 90% N₂ for 1 hour followed by pure H₂ for 1 hour on the fuel electrode. On the oxygen electrode, air flow was maintained. Following this reduction, initial electrochemical characterization of the cells was performed. Cell-A was used for initial electrochemical characterization (fingerprint) only, while Cell B was tested galvanostatically and Cell-C and Cell-D were tested potentiostatically. The fingerprint can be defined as an electrochemical characterization of the cells at various temperatures ranging from 800 °C, 750 °C, 700 °C and 650 °C such that i-V characterization and EIS measurements were performed with either air or O₂ being supplied to the oxygen electrode, while changing the steam content to 4%, 20%, 50%, 80% and 90% with H₂ on the fuel electrode. For the co-electrolysis characterization, gas mixtures of 40% H₂O + 50% CO₂ + 10% H₂, 45% H₂O + 45% CO₂ + 10% H₂ and 65% H₂O + 25% CO₂ + 10% H₂ were supplied to the fuel electrode. For the EIS measurements, a Solartron 1255 frequency analyzer with an external shunt resistor in series with the cell was used at zero DC current. EIS was recorded from 96850 to 0.08 Hz with 12 points per decade. A correction using the short circuit impedance response of the test setup was performed. From the EIS, the real part at 96850 Hz was treated as the ohmic resistance (Rₛ) while the polarization resistance (Rₚ) was then calculated as the difference in the real part of the impedance at 96850 Hz and 0.08 Hz. i-V curves were recorded both in the fuel cell (FC) and the electrolysis (EC) mode such that for the FC mode, the minimum voltage limit was set to 650 mV, while for EC mode the maximum voltage was set to 1300 mV.

The electrochemical durability testing of the SoA cells was carried out with the fuel electrode gas composition of 65% H₂O + 25% CO₂ + 10% H₂ and with O₂ on the
2.3 Results and Discussion

2.3.1 Electrochemical Analysis

Four SoA cells were tested with the following conditions:

- Cell-A: Initial characterization only
- Cell-B: Durability test under galvanostatic condition for 1000 hours
- Cell-C: Durability test under potentiostatic condition for 500 hours
- Cell-D: Durability test under potentiostatic condition for 1000 hours

The cells were tested under co-electrolysis conditions and the initial performance is compared in the i-V plot in Figure 2.1. This was at the initial characterization stage when the cell was reduced at 800 °C and then characterization at 750 °C was performed. All the cells exhibit similar performance until 0.6 A/cm². However, Cell-D deviates significantly at higher current densities, especially over 0.8 A/cm².

The i-V curves were drawn again prior to starting the durability test as shown in Figure 2.2. A change in the performance of Cell-C and Cell-D was observed. Cell-D, moreover, shows significant deviation. According to the i-V curves, thermoneutral operation at 1.33 V under co-electrolysis conditions could lead to high current densities leading to a high overpotential for the cells. As a result, an operating voltage of 1.2 V is chosen which corresponds to 0.75 A/cm² for Cell-B which is operated galvanostatically. Cell-C and Cell-D were operated potentiostatically. Due to the voltage...
control issues during potentiostatic testing, Cell-C could only be operated until 500 hours and displayed severe degradation, while Cell-D was operated for 1000 hours.

**Figure 2.1:** $i$-$V$ curves during the initial characterization with $65\% \text{H}_2\text{O} + 25\% \text{CO}_2 + 10\% \text{H}_2$ on the fuel electrode and $\text{O}_2$ on the oxygen electrode at $750 ^\circ \text{C}$.

**Figure 2.2:** $i$-$V$ curves just before the durability testing with $65\% \text{H}_2\text{O} + 25\% \text{CO}_2 + 10\% \text{H}_2$ on the fuel electrode and $\text{O}_2$ on the oxygen electrode at $750 ^\circ \text{C}$.

The evolution of the cell voltage for Cell-B was plotted in Figure 2.3. It is visible that the cell voltage increases rapidly in the first 200 hours of testing and thereafter
stabilizes. For the case of potentiostatic testing, evolution of the current density for both Cell-C and Cell-D are plotted in figure 2.4. In this case as well, a rapid decrease of current density is observed for the first 200 hours which stabilizes thereafter. This gives an indication of the degradation mechanisms which is similar for both modes of testing. For Cell-C, due to the potentiostatic control issues with the setup, a sudden decrease in the current density is seen, and the cell attains current density as low as 0.2 A/cm$^2$ during the initial 200 hours depicting severe degradation. As a result, the cell was only operated for 500 hours only.

Comparing Figure 2.3 and Figure 2.4, Cell-B and Cell-C have similar starting point of 0.75 A/cm$^2$ at 1200 mV. However, after 200 hours, Cell-C starts to degrade significantly. Cell-D has a lower operating current density throughout the test. Regardless, the evolution trend is similar for both testing modes. Since the initial voltage and current density showed significant disparity, the relative change in the long-term operation would lead to the identification of degradation mechanisms.

**Figure 2.3:** The evolution of the cell voltage during the galvanostatic testing-Cell-B with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C at a current density of 0.75 A/cm$^2$. 
2.3 Results and Discussion

Figure 2.4: The evolution of the current density during the potentiostatic testing—Cell-C and Cell-D with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C at 1.2 V.

Regardless of the fact that the performance of Cell-D was inferior to Cell-B and Cell-C, the relative change in Area specific resistance (ASR) degradation is compared in this chapter. ASR can serve as a measure of relative change in cell performance due to change in resistance of the cell which also relates to the reaction mechanism. ASR is calculated as:

\[ ASR = \frac{O\text{CV} - V}{I} \] (2.1)

where, OCV is the open circuit voltage of the cell, V is the measured operating voltage, and I is the measured current density.

The calculated ASR was thereafter split into ohmic resistance (R$_s$) and polarization resistance (R$_p$) with the help of EIS under current, to understand the evolution depending on the mode of operation. The ohmic resistance predominantly describes the influence of electrolyte and contact resistance, while the polarization resistance takes into account the influence of reactions at TPB, charge transfer, gas composition and influence of diffusion of the ions. This is displayed in the Figure 2.5. For the galvanostatic testing, both R$_s$ and R$_p$ increase with time, while for potentiostatic testing, only R$_p$ seems to increase. Interestingly, for Cell-C, the degradation is clearly reflected in both R$_s$ and R$_p$. This indicates severe irreversible degradation of the cell which might be seen in the form of delamination of layers of the cell. Since the potentiostatic operation should result in
only increase of $R_p$ [28], $R_s$ increase due to voltage control observed during testing is an indication of an overshoot of overpotential which led to the degradation of Cell-C.

Figure 2.5: Breakdown of the ASR obtained from EIS under current, with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

It was of particular interest to analyze the degradation of the electrodes in terms of the overpotential experienced. Overpotential can be defined as the change in the potential experienced by the electrodes of the cell in comparison to the potential in equilibrium is the overpotential [37]. Overpotential is calculated according to the following equation:

$$O_p = V - OCV$$  \hspace{1cm} (2.2)

where, $V$ is the measured cell voltage under current, and $OCV$ is the measured open circuit voltage.

The overpotentials were similar and are listen in the Table 2.1.

Table 2.1: Overpotential for the different cell tests.

<table>
<thead>
<tr>
<th>Test</th>
<th>Overpotential at the beginning of the test</th>
<th>Overpotential at the end of the test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell-B (Galvanostatic)</td>
<td>303 mV</td>
<td>552 mV</td>
</tr>
<tr>
<td>Cell-C (Potentiostatic)</td>
<td>329 mV</td>
<td>331 mV</td>
</tr>
<tr>
<td>Cell-D (Potentiostatic)</td>
<td>329 mV</td>
<td>328 mV</td>
</tr>
</tbody>
</table>
For Cell-B, a significant increase in the overpotential is seen since the cell voltage increases throughout the testing period, while for the cells tested potentiostatically, the overpotential remains constant. For the galvanostatic operation, high overpotentials have been reported to cause severe degradation [16]. This implies that the potentiostatic mode of operation results in protecting the cell from a high overpotential by decreasing the current density.

Moreover, to understand the behavior of the cells, i-V curves were plotted before and after the long-term test for each cell. This is shown in Figures 2.6, 2.7 and 2.8.

**Figure 2.6:** i-V curves before and after the durability testing for Cell-B with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

**Figure 2.7:** i-V curves before and after the durability testing for Cell-C with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.
All the cells degrade during testing. However, for Cell-B an OCV change of 5 mV was observed after testing, while for Cell-C the OCV change was 44 mV, and for Cell-D, no OCV change was observed after testing. For Cell-B, the current density obtained at 1.3 V is reduced from 1 A/cm² to 0.6 A/cm² after durability test, while for Cell-C the current density decrease to approximately 0.08 A/cm² indicating severe degradation due to the incident of control failure indicated earlier in the text. For Cell-D, the current density decreased from 0.85 A/cm² to approximately 0.7 A/cm².

Since the $R_s$ remains constant for the case of potentiostatic testing, change in polarization resistance could be compared for both modes of testing to understand the difference in the degradation mechanisms of the cells. For the case of galvanostatic testing, $R_p$ is also compared while the degradation also affected the $R_s$.

To analyze the polarization resistance, distribution of relaxation times (DRT) was used. Gas shifts were performed such that by changing the gas on the fuel electrode while keeping the oxygen electrode gas unchanged, the fuel electrode response was identified. Similarly, by changing the gas on the oxygen electrode from oxygen to air while keeping the gas on the fuel electrode unchanged, the oxygen electrode response was identified. This is mentioned in detail in Manuscript-1. The corresponding frequencies for the electrode response can be seen in Table 2.2. Simultaneously, the overpotentials were calculated as listed previously in the Table 2.1. DRT analysis was performed for the three tests to identify the cause and extent of degradation. In the Figures 2.9, 2.10 and 2.11, DRT plots before and after the long-term test at OCV are displayed for all three cells.
Table 2.2: Identification of characteristic frequency for SoA cell.

<table>
<thead>
<tr>
<th>No.</th>
<th>Process</th>
<th>Relaxation frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gas conversion</td>
<td>1-3 Hz</td>
</tr>
<tr>
<td>2</td>
<td>Diffusion</td>
<td>30-50 Hz</td>
</tr>
<tr>
<td>3</td>
<td>Fuel and oxygen electrode</td>
<td>100-1000 Hz</td>
</tr>
<tr>
<td>4</td>
<td>Fuel and oxygen electrode, TPB processes</td>
<td>1-8 kHz</td>
</tr>
<tr>
<td>5</td>
<td>Fuel electrode, oxygen ion transport</td>
<td>18-20 kHz</td>
</tr>
</tbody>
</table>

Figure 2.9: EIS and DRT plots before and after the durability testing for Cell-B with 65% H₂O + 25% CO₂ + 10% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C.

For Cell-B, Nyquist plot in Figure 2.9 clearly indicates change in both $R_s$ and $R_p$. For the identification of electrode responsible for degradation of $R_p$, DRT plot indicates a change in response at frequencies of 200-500 Hz, 5-8 kHz and 20 kHz. This corresponds to the degradation of both the fuel and the oxygen electrode but an additional contribution from the fuel electrode at frequency of 20 kHz. Literature studies have reported the degradation of the fuel electrode under galvanostatic conditions due to high overpotential [16], which correlates to the results obtained in this work.
For Cell-C, Nyquist plot in Figure 2.10 indicates a huge difference between the impedance plots both in $R_s$ and $R_p$ making it difficult to compare with the impedance spectra at the beginning of test. DRT plot indicates an increase in response at frequencies of 300-500 Hz as well as 5-8 kHz related to the degradation of both the fuel and the oxygen electrode. A comprehensive understanding of degradation mechanisms is difficult due to the severe increase in the ASR which indicates the degradation of microstructure.

For Cell-D, Nyquist plot in Figure 2.11 indicates clear increase in $R_p$, while $R_s$ change is marginal. The degradation of the cell results from both oxygen and fuel electrode reactions as can be seen from DRT plot. At the frequencies of 500-800 Hz and 1 kHz, change in the electrode response is seen. It should be taken into account that the frequency response shifts towards lower frequencies after degradation. It is worth noting that the additional response at frequency of 20 kHz is not seen in the case of potentiostatic testing leading to a different extent of the degradation mechanism on the fuel electrode.

![Figure 2.10: EIS and DRT plots before and after the durability testing for Cell-C with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.](image-url)
2.3 Results and Discussion

Figure 2.11: EIS and DRT plots before and after the durability testing for Cell-D with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

From the DRT analysis, both the fuel and the oxygen electrode seem to degrade. However, in Manuscript-2, a more detailed analysis relating to the influence of leaks in the setup indicates a major contribution from the oxygen electrode towards the degradation of the cell.

2.3.2 Microstructural Analysis

Post-test microstructural analysis was performed for Cell-B and Cell-D. Cell-C, due to severe degradation, was noticed to be oxidized on cooling down, as well as broken completely. As a result, SEM analysis was not performed on Cell-C. It was of particular interest to look into both fuel and oxygen electrode degradation for Cell-B and Cell-D. For this, low voltage SEM analysis was performed at 1 kV through In-lens detector to see the connectivity of Ni particles [36]. This is called percolation wherein, the bright particles are the conducting Ni particles while non-conducting Ni along with YSZ and pores is seen as dark particles. Complimentary to In-lens imagining, SE-2 detector was also engaged to look at the microstructure in order to investigate the layers and their adhesion in particular.

SEM images for Cell-B is shown in Figure 2.12. Here, the oxygen electrode is on top, followed by the barrier layer, the electrolyte and the fuel electrode. In Figure
2.3 Results and Discussion

2.12(a), the circles indicate the loss of percolation or active Ni particles in the vicinity of the electrolyte. This conclusion is drawn based on the reference cell Ni percolation data which can be found in Manuscript-1. This indicates a loss of active Ni leading to contribution from the fuel electrode towards degradation of the cell. In Figure 2.12(b), a delamination of the barrier layer from the electrolyte is seen indicating the degradation of the oxygen electrode as well as increase in $R_s$. Since the OCV did not change significantly during testing, it is indicated that the interface may have weakened during testing.

![Figure 2.12](image)

**Figure 2.12:** Post-test (a)In-lens, and (b)SE-2 SEM images for Cell-B taken at 1 kV.

SEM images for Cell-D is shown in Figure 2.13. Cell-D displayed higher ASR than the other cells at the beginning of durability test. However, no change in OCV was observed during testing. Since the electrochemical analysis points to the degradation of the fuel electrode, percolation analysis was performed for Cell-D as shown in Figure 2.13(a) and (b). Clearly, the loss of active Ni particles is seen close to the electrolyte. In Figure 2.13(c), SE-2 images shows vertical cracks in the cell. Since the OCV is constant throughout the testing period, the cracks seem to spread after the end of the durability test. This leads to the oxidation of the fuel electrode locally, where the cracks are formed and a loss of adhesion between all the layers is visible.
2.4 Conclusions

In this work, the cells were tested for durability in galvanostatic and potentiostatic modes for a comparison of the degradation mechanisms during co-electrolysis of steam and CO\textsubscript{2} intended at rendering syngas for methane production. Preliminary analysis indicated similar trend in degradation of cells during both modes of testing. In the initial 200 hours, there was a rapid degradation of the cell followed by stabilization in the next 800 hours of testing. However, in case of galvanostatic testing for Cell-B both R\textsubscript{s} and R\textsubscript{p} increased over the course of durability testing. This resulted in an increase of overpotential which led to increased degradation. On the other hand, in potentiostatic testing pertaining to Cell-D, only R\textsubscript{p} increased while R\textsubscript{s} remained constant as a result of the constant overpotential experienced by the cell. For Cell-C, the control issues led to severe degradation of cell which is seen in the form of huge increase in R\textsubscript{s} and R\textsubscript{p}. DRT analysis indicated degradation of both the electrodes. However, more influence of the oxygen electrode was inferred from the leak analysis. In conclusion, potentiostatic mode of operation serves to limit the degradation by protecting the cell by maintaining the overpotential experienced by the cell contrary to the case of galvanostatic testing.

Figure 2.13: Post-test (a)In-lens, (b)In-lens, and (c)SE-2 SEM images for Cell-D taken at 1 kV.
Durability testing-modification in electrode structure

3.1 Introduction

In the previous chapter, it has been demonstrated that the use of potentiostatic mode of testing over a long-term can protect the cell from accelerated degradation by maintaining a constant overpotential. However, for the SoA cells, severe degradation was seen in the case of potentiostatic testing. This led to the investigation of the electrode structures to enhance the performance and the lifetime of SOECs. This chapter comprises of results published in Manuscript-2.

Literature studies have reported the degradation of the oxygen electrode activity related to the oxygen evolution reaction \([20, 21]\). This has been previously investigated via various techniques regarding fabrication of the electrode \([21]\). In particular, optimization of the oxygen electrode through infiltration on a porous backbone structure has been previously reported \([38, 39]\). Moreover, different types of composites as well as mixed ionic electronic conductors (MIECs) have also been reported in literature to have an impact on the degradation mechanisms \([27]\). Regarding the degradation of the Ni-YSZ fuel electrode, presence of impurities, loss of Ni percolation and migration, coarsening of Ni particles have been investigated in literature \([16, 18, 19]\). Recent advances in the fuel electrode development have also been reported to play a major role in the durability of the SOECs \([40]\).

In this work, the initial performance of four different types of fuel electrode supported cells are characterized and the results are discussed. Three of these cell types, except Cell-4, were also analyzed for degradation after durability testing. Cell-1 and Cell-3 were tested for 1000 hours while Cell-3 was tested only for approximately 500 hours. The three cells were tested potentiostatically at 1.2 V for durability studies. The difference in the degradation mechanisms relating to electrode structure is addressed through electrochemical and microstructural analysis.

3.2 Experimental

Four cells comprising of different electrode structures were studied in this work. Cell-1 was a SoA cell, as described in previous chapter. Cell-2 was prepared by infiltrating the LSC particles on CGO backbone on a half cell consisting of Ni-YSZ fuel electrode and support, YSZ electrolyte and CGO barrier layer. 1M LSC solution was infiltrated for 9 cycles such that after every cycle, the cell was placed in the furnace at 350 °C for
one hour and then cooled down. Cell-3 was prepared by optimizing the fuel electrode porosity and particle size distribution [16]. This cell contains a composite LSC-CGO oxygen electrode. Cell-4 consists of LSCF-CGO oxygen composite electrode on top of the half cell used in Cell-2 and Cell-3. A sketch of the cell layout can be seen in Figure 3.1.

![Figure 3.1: Sketch showing the different layers of the SOECs tested in this work for durability analysis [29], Cell A=Cell-1, Cell B=Cell2 and Cell C=Cell-3.](image)

The cells were mounted in an alumina test house with gold on the oxygen side and nickel on the fuel side for current collection, along with a gold sealing on the fuel side. A 4 kg weight was applied to ensure leak tight setup. Details of the setup are described in literature [32, 33].

These four cell types were initially characterized at various temperatures. For Cell-1, the cell was reduced at 800 °C and characterization was carried out at 800, 750, 700 and 650 °C. For Cell-2, Cell-3 and Cell-4, the cells were reduced at 850 °C with 5% H₂ and remaining N₂ being fed to the fuel electrode, and air on the oxygen electrode for 2 hours. Thereafter, the characterization was carried out at 850, 800, 750 and 700 °C. During the characterization, the following gas compositions were fed on the fuel electrode:

- 4% H₂O + 96% H₂
- 20% H₂O + 80% H₂
- 50% H₂O + 50% H₂
- 80% H₂O + 20% H₂
On the oxygen electrode, air or O\textsubscript{2} was fed during characterization. i-V curves were drawn under each operating condition both in fuel cell (FC) and electrolysis (EC) modes. In the FC mode, the cut-off cell voltage was 700 mV, while for the EC mode the cut-off was 1300-1400 mV.

A Solartron 1255 frequency analyzer with an external shunt resistor in series with the cell at zero DC current was used for EIS measurements, such that the spectra were recorded from 96850 to 0.08 Hz with 12 points per decade. A correction for the setup was performed using the short circuit impedance response. The real part of the spectra at 96850 Hz was treated as the ohmic resistance (R\textsubscript{s}). Additionally, the difference in the real part of the impedance between 96850 Hz and 0.08 Hz was treated as the polarization resistance (R\textsubscript{p}).

Durability tests were performed for Cell-1, Cell-2, and Cell-3 at 750 °C, 1.2 V with 65% H\textsubscript{2}O + 25% CO\textsubscript{2} + 10% H\textsubscript{2} on the fuel electrode and O\textsubscript{2} on the oxygen electrode. The test was stopped when the current density reached 0.3 A/cm\textsuperscript{2}. Data analysis was performed using Ravdav software [34].

In addition, the post-test scanning electron microscopy (SEM) analysis was performed using Supra-35 scanning electron microscope equipped with a field emission gun (FE-SEM, Carl Zeiss) and an energy-dispersive X-ray spectrometer (EDX, Thermo Electron Corporation). Images were obtained at 5 kV. In addition, low voltage (LV) SEM through an In-lens detector and an accelerating voltage of 1 kV was considered [36].

### 3.3 Results and Discussion

#### 3.3.1 Electrochemical analysis

The four cells were characterized under co-electrolysis conditions at 750 °C and i-V curves are compared in Figure 3.2. Here, Cell-1 serves as the benchmark with approximately 0.9 A/cm\textsuperscript{2} at 1300 mV. The performance of Cell-2 deviated significantly from Cell-1, already at a low current density of 0.2 A/cm\textsuperscript{2}, reaching a current density of 0.7 A/cm\textsuperscript{2} at 1300 mV. The performance of Cell-3, on the other hand, showed significant improvement than Cell-1 especially at current densities over 0.5 A/cm\textsuperscript{2}, achieving a current density of 1.1 A/cm\textsuperscript{2} at 1300 mV. Cell-4 performed similar to Cell-2.
3.3 Results and Discussion

Figure 3.2: i-V curves during the initial characterization with 65% H₂O + 25% CO₂ + 10% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C.

This indicates enhanced performance of Cell-3. However, for Cell-2 and Cell-4, a lower performance than Cell-1 (SoA cell) was observed. To analyze the difference in initial performance of the cells, EIS spectra are compared in Figure 3.3. Interestingly, all the cells have different Rₛ and Rₚ. The difference in Rₛ can be attributed to the contact of the cell with the gas flow channels, as well as the temperature of operation. Furthermore, the different oxygen electrodes also contribute to the Rₛ. Cell-3 has the lowest Rₛ while Cell-2 and Cell-4 have the highest Rₛ. For the case of Rₚ, Cell-3 has higher Rₚ than Cell-1. However, this is predominantly reflected in the form of conversion arc which is indicated to be a result of presence of leaks. This is also observed for Cell-4, where significant leaks are present.

To compare the effect of gas conversion, Figure 3.4 displays a bode plot where around frequencies of approximately 1 Hz, a significant difference in conversion arc on the fuel electrode is visible. Furthermore, at frequencies of approximately 5-10 kHz, a change in electrode response is seen which makes the cells difficult to compare.

As an indication of the leak, the difference between OCV and theoretical value was considered. This was then converted in the form of excess O₂ in the fuel stream and leak current, according to the following equations.

\[
\text{Number of moles} = \frac{\text{excess } O_2 (L/h)}{22.4}
\]

\[
\text{Leak current} = \frac{\text{Number of moles} (mol/h) \times F (A \text{ s/mol}) \times 4}{3600 \times 16 \text{ cm}^2}
\]
where, \( F \) is the Faraday constant, and \( 4 \) refers to the number of electrons per mole of excess \( O_2 \) gas.

The calculated leak current, pertaining to the cell OCV is given in Table 3.1.

**Figure 3.3:** EIS during the initial characterization with 65% \( H_2O \) + 25% \( CO_2 \) + 10% \( H_2 \) on the fuel electrode and \( O_2 \) on the oxygen electrode at 750 °C.

**Figure 3.4:** Bode plot during the initial characterization with 65% \( H_2O \) + 25% \( CO_2 \) + 10% \( H_2 \) on the fuel electrode and \( O_2 \) on the oxygen electrode at 750 °C.

**Table 3.1:** Calculation of the leaks in the cell setup (65 %\( H_2O \) + 25% \( CO_2 \) + 10% \( H_2 \) at the fuel electrode, \( O_2 \) at the oxygen electrode, at 750 °C).

<table>
<thead>
<tr>
<th>Cell</th>
<th>Difference in OCV / mV</th>
<th>Corresponding leak current before/ mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell-1</td>
<td>5</td>
<td>38</td>
</tr>
<tr>
<td>Cell-2</td>
<td>7</td>
<td>47</td>
</tr>
<tr>
<td>Cell-3</td>
<td>13</td>
<td>65</td>
</tr>
<tr>
<td>Cell-4</td>
<td>13</td>
<td>65</td>
</tr>
</tbody>
</table>
Cell-1 has the minimum leak, while Cell-3 and Cell-4 have the maximum leak. The additional area specific resistance (ASR) contribution for Cell-2 arises from the $R_s$. The $R_p$, excluding the conversion resistance (the arc at low frequency), was the lowest for Cell-3 and the highest for Cell-4.

The aim of this work was to achieve an enhanced performance when compared to the SoA cell, which was not the case for Cell-4. Cell-2 already serves as a candidate for the modification of the oxygen electrode. All the cells, except Cell-4 were tested for durability at 1.2 V potentiostatically. As stated in the previous chapter, this protects the cell by lowering the current density. In this chapter, an evaluation of the degradation mechanisms pertaining to both fuel and oxygen electrode modification was performed, by comparing Cell-1 with Cell-3 and Cell-4 respectively. The evolution of current density is explained in Manuscript-2. Since the cells have different current densities at the beginning of durability testing, the evolution of the ASR is of essence relating to the degradation of electrodes in particular as shown in Figure 3.5. The ASR is calculated as the ratio of difference between theoretical cell voltage and OCV, and current density as described in previous chapter.

In line with the initial characterization, Cell-3 has lower ASR than Cell-1, while Cell-2 has higher ASR. Moreover, already at the beginning of durability test, there was a difference in ASR values which may affect the degradation mechanisms. It is interesting to note from Figure 3.5, that the degradation of Cell-1 and Cell-2 follow similar trend where there is higher degradation in the initial 200 hours of testing which stabilizes in the rest of the test. This indicates similar underlying mechanisms for degradation. For Cell-3, the degradation trend is linear throughout the test indicating gradual degradation.
3.3 Results and Discussion

Figure 3.5: The evolution of the ASR during durability analysis with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

To comprehend the degradation mechanisms, $R_p$ was further analyzed through EIS and DRT investigations. Since the $R_s$ does not change significantly during potentiostatic testing, $R_p$ serves as an indicator of degradation. More details on the DRT analysis in detail can be found in Manuscript-2. In Table 3.3, the relaxation frequencies of the processes corresponding to individual electrode have been listed.

Table 3.2: DRT gas shift analysis for the identification of the electrode response.

<table>
<thead>
<tr>
<th></th>
<th>Process</th>
<th>Relaxation frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cell-1</td>
</tr>
<tr>
<td>1</td>
<td>Gas conversion</td>
<td>1-3 Hz</td>
</tr>
<tr>
<td>2</td>
<td>Diffusion</td>
<td>30-50 Hz</td>
</tr>
<tr>
<td>3</td>
<td>Oxygen electrode</td>
<td>100-1,000 Hz, 1-8 kHz</td>
</tr>
<tr>
<td>4</td>
<td>Fuel electrode, TPB processes</td>
<td>100-1,000 Hz, 1-8 kHz</td>
</tr>
<tr>
<td>5</td>
<td>Fuel electrode, oxygen ion transport</td>
<td>18-20 kHz</td>
</tr>
</tbody>
</table>

For Cell-1, the characteristic frequencies for the fuel and the oxygen electrode overlap in the range of 100-1000 Hz.

Once the electrode frequencies were identified, the evolution of $R_p$ under current was considered to identify a change in processes relating to degradation. For
3.3 Results and Discussion

Cell-1, Figure 3.6 represents the EIS and DRT at an interval of approximately 200 hours throughout the course of durability testing. Since the conversion arc changes significantly, it is difficult to conclude the degradation of electrodes with certainty. However, the processes within frequencies from 100-1000 Hz seem to degrade. Since this is the same SoA cell which was discussed in the previous chapter, the frequencies agree with the ones discussed earlier, corresponding to the degradation of both the fuel and the oxygen electrode. However, due to the presence of the leaks in test setup, change of leak was also plotted in Manuscript-2. This clearly shows a major change due to the oxygen electrode contribution.

![Graph showing EIS and DRT for Cell-1](image)

**Figure 3.6:** The evolution of the EIS and DRT during durability for Cell-1 with 65% H₂O + 25% CO₂ + 10% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C.

Similarly, in Figure 3.7 the EIS and DRT analysis for Cell-2 is presented. Since the cell showed high ASR from the beginning, the operating current density during the durability test varied from 0.33 to 0.22 A/cm², making the comparison of EIS feasible due to relatively small change in the conversion arc. Here, a high degradation at approximately 200 Hz is seen, corresponding to the oxygen electrode under current. A change in frequency around 1 kHz is also visible, corresponding to the fuel electrode. However, the major contribution is attributed to the degradation of
the oxygen electrode. This implies that the infiltration of the oxygen electrode was not optimal. Moreover, since both Cell-1 and Cell-2 degrade predominantly due to the oxygen electrode the degradation trends are similar. This indicates the effect of a poor oxygen electrode on the cell performance, regardless of the difference in the fuel electrode structure.

For Cell-3, the evolution of the EIS and DRT is shown in Figure 3.8. There is a significant difference in the current densities during durability testing leading to a change in conversion arc. However, an increase in frequency response at approximately 1 kHz is prominent corresponding to the fuel electrode. This was also confirmed through leak analysis in Manuscript-2. This indicates a rather different degradation mechanism than the other two cells. It is also interesting to see a change in $R_s$ during testing which might be due to the increase of leaks. This refers to the stressing of the cell since the cell experiences higher overpotential than it would if the OCV was close to theoretical value.

![Figure 3.7](image.png)

**Figure 3.7:** The evolution of the EIS and DRT during durability for Cell-2 with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

Both Cell-2 and Cell-3 experienced an increase in leak during the durability test. Additionally, both the cells have similar fuel electrode structure which is different from Cell-1. Regardless, the electrochemical analysis indicates the degradation of the oxygen electrode for Cell-1 and Cell-2 implying that the most of the overpotential was
experienced by the oxygen electrode, while for Cell-3 the fuel electrode experienced most of the cell overpotential, along with the contribution of leaks.

![Graph showing EIS and DRT evolution](image)

**Figure 3.8:** The evolution of the EIS and DRT during durability for Cell-3 with 65% H₂O + 25% CO₂ + 10% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C.

### 3.3.2 Microstructural analysis

Post-test SEM analysis was carried out for the four cells to correlate the performance with the structure of the electrodes. For Cell-1 and Cell-2, the emphasis was on the degradation of the oxygen electrode, while for Cell-3 analysis of the fuel electrode was treated in detail. For Cell-4, an overview of the cell structure with emphasis on adhesion of the layers was investigated.

An overview of all the four cells is displayed in Figure 3.9. For all the cells, the oxygen electrode is on top, followed by CGO barrier layer, YSZ electrolyte and Ni-YSZ fuel electrode (active and support). Cell-1 has a different fuel electrode structure than the remaining three cells. All the cells have different oxygen electrodes. It is interesting to see that the cracks were observed in the case of Cell-1 after durability testing, as explained in the previous chapter. For Cell-4, a clear lack of adhesion is
seen between the CGO barrier layer and the LSCF oxygen electrode leading to an abrupt delamination which can be indicated as the cause of the low electrochemical performance of the cell.

Figure 3.9: SE-2 SEM images displaying an overview of (a) Cell-1, (b) Cell-2, (c) Cell-3, and (d) Cell-4 at 5 kV.

For comparison of the oxygen electrode, Cell-2 is analyzed for non-optimized infiltration. A comparison is drawn between Cell-1 and Cell-2. Figure 3.10(a) displays SoA cell with LSCF-CGO composite oxygen electrode. In Figure 3.10(b) and (c), islands of infiltrates can be seen while a network of LSC particles on the CGO backbone from the barrier layer is not clearly visible indicating discontinuity leading to low performance of the oxygen electrode. For Cell-4, a discontinuity between the interfaces of CGO barrier layer and LSCF oxygen electrode is highlighted in Figure 3.10(d). This is in agreement with the electrochemical analysis.
3.3 Results and Discussion

Figure 3.10: SE-2 SEM images displaying oxygen electrode for (a) Cell-1, (b) Cell-2, (c) Cell-2 (zoomed in), and (d) Cell-4 at 1 kV.

For analyzing the fuel electrode, Cell-1 and Cell-3 are compared in Figure 3.11. Clearly there is a difference in structure of the fuel electrode. The active fuel electrode is optimized for Cell-3 as stated in literature [16].

Figure 3.11: In-lens SEM images displaying the fuel electrode for (a) Cell-1, (b) Cell-3, and (c) sister cell to Cell-3 at 1 kV.

Moreover, to analyze the degradation of Cell-3 a sister cell was tested for initial characterization only. This was then compared for percolation analysis with Cell-3 after durability testing in figure 3.11(b) and (c). A loss of the active Ni network is visible in the vicinity of the electrolyte, highlighted in Figure 3.11(b). This also indicates the migration of Ni particles toward the support away from the electrolyte.
due to high humidity content. Detailed qualitative analysis of Ni migration for Cell-3 can be found in Manuscript-2. Cell-3 also presents with the inter-granular cracks due to the presence of high leak rate throughout the test which leads to weakening of interfaces and post-test cracks.

3.4 Conclusions

Four cells with a variation in electrode structure and composition were tested to comprehend the dependency of the degradation mechanisms on the cell type. Electrode modifications related to the oxygen electrode led to a decrease in performance compared to SoA cell, due to non-optimized infiltration in case of Cell-2, and a lack of adhesion between oxygen electrode and the barrier layer, in case of Cell-4. On the other hand, the fuel electrode modification led to a significant improvement in the cell performance and durability. The degradation of the fuel electrode in terms of Ni migration resulting in loss of percolation was indicated.
4.1 Introduction

Use of renewable energy for power production is accompanied by the need of energy storage due to the intermittent nature of the energy being produced. For instance, the wind turbines depend on the wind profile, which leads to a mismatch in the integration of the renewable power production with the grid, since a specific power profile is desired [6, 41]. The energy storage in dynamic context is of utmost importance and in this work, a dynamic load profile testing was applied on the cell and the stack level to propagate the results of the testing modes and modifications performed so far. This chapter is based on Manuscript-3. In the previous chapters, the need for improvement of performance and durability of SOECs have been discussed. Electrode modifications led to the development of an improved cell structure. This cell type serves as a candidate for the future tests involving dynamic cycling.

Conventional technologies for energy storage such as hydro, air pumps and batteries have been investigated widely in literature [4, 41]. SOECs are upcoming in the field of large scale energy storage, owing to the storage efficiency as well as the versatility in the context of hydrocarbon storage [42].

In this chapter, a simulated wind profile imitating the wind pattern recorded at the island of Bornholm was used for testing SOECs [43]. Firstly, the improved cell was tested under co-electrolysis to comprehend the degradation. Following this, a stack with 6 similar improved cells was tested under co-electrolysis with dynamic wind profile. The simulated wind profile for both the cell and the stack are displayed in Figure 4.1. The similarity and differences in testing as well as degradation are highlighted in this chapter for an optimal production of syngas under durable conditions.
4.2 Experimental

4.2.1 Cell test

The improved cell described in previous chapter was tested under dynamic wind conditions. The cell consists of LSC-CGO oxygen electrode with CGO barrier layer, YSZ electrolyte, Ni-YSZ active fuel electrode and support. Ni-YSZ structure ratio has been optimized in terms of porosity and particle size distribution [16]. The cell was tested in an alumina test house as described in literature [32, 33]. Gold on the oxygen side and nickel on the fuel side act as current collectors. A gold sealing was also used on the fuel side. Furthermore, 4 kg of weight was applied to ensure a leak tight setup. The cell was reduced at 850 °C with 5% H₂ and remaining N₂ being fed to the fuel electrode, and air on the oxygen electrode for 2 hours. Thereafter, the characterization was carried out at 850, 800, 750 and 700 °C.

i-V curves were drawn such that in the FC mode, the minimum voltage was 700 mV while for the EC mode the maximum cell voltage was 1300 mV. For the impedance measurement, a Solartron 1255 frequency analyzer with an external shunt resistor in series with the cell at zero DC current was used. The recording of the spectra was performed from 96850 to 0.08 Hz, and 12 points per decade. A correction for the setup was performed using the short circuit impedance response. The real part of the spectra at 96850 Hz was treated as the ohmic resistance (R_s), while the difference in the real part of the impedance 96850 Hz and 0.08 Hz was treated as the polarization resistance (R_p).
The durability test was performed with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode. Data analysis was performed using Ravdav software [34].

Moreover, the post-test scanning electron microscopy (SEM) analysis was performed using Supra-35 scanning electron microscope equipped with a field emission gun (FE-SEM, Carl Zeiss) and an energy-dispersive X-ray spectrometer (EDX, Thermo Electron Corporation). Images were obtained at 15, 10, 5 kV using SE-2 and backscatter detectors. In addition, low voltage (LV) SEM through an In-lens detector and an accelerating voltage of 1 kV was considered [36].

4.2.2 Stack test

A stack with six cells, similar to the one described earlier in this section was manufactured by SOLIDPower. It was tested under co-electrolysis conditions. The fuel electrode of the cells in stack was pre-reduced when received. The cell active area was 80 cm$^2$. The setup for stack testing has been described previously in literature [44]. Initial characterization of the cells in the stack was performed with 20%, 50%, 80%, 90% H$_2$O with remaining H$_2$% on the fuel electrode and O$_2$ and air on the oxygen electrode. For the co-electrolysis characterization, 45% CO$_2$ + 45% H$_2$O + 10% H$_2$, and 25% CO$_2$ + 65% H$_2$O + 10% H$_2$ were fed to the fuel electrode, with O$_2$ and air on the oxygen electrode. i-V curves were recorded in both the FC and the EC modes with a maximum current density of 0.5 A/cm$^2$. The wind profile was modified for the stack test for this current density limit.

A Solartron 1252A frequency analyzer was used for impedance measurements, with a Kepco BOP 50-4M which was used to boost the 16 mA AC current from the Solartron to 1A AC and an external current transducer in series with the cell. EIS was recorded from 96850 to 0.08 Hz with 12 points per decade and was corrected using the short circuit impedance response of the test setup. The ohmic resistance (R$_s$) was taken as the value of the real part of the impedance at 25 kHz, while the polarization resistance (R$_p$) was then calculated as the difference in the real part of the impedance at 25 kHz and 0.1 Hz.

During the durability test, 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ was supplied to the fuel electrode with O$_2$ on the oxygen electrode. EIS measurements on the single cells during the dynamic durability tests were carried out at 0.4 A/cm$^2$ for the stack. EIS was also recorded at 0.25 A/cm$^2$ for the stack. Analysis of the impedance data was performed using the software Ravdav [34].
4.3 Results and Discussion

4.3.1 Cell testing

4.3.1.1 Electrochemical Analysis

The cell was initially characterized at 750 °C under co-electrolysis conditions to analyze the performance as displayed in Figure 4.2. At 1300 mV, a current density of approximately 1 A/cm$^2$ was attained as shown in Figure 4.2(a). The cell OCV was 868 mV which is 29 mV lower than the theoretical OCV, indicating leaks. This is seen in the conversion arc of EIS in Figure 4.2(b).

![Figure 4.2: i-V and EIS during the initial characterization with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode, at 750 °C.](image)

This cell was thereafter tested with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode and 750 °C for durability testing by varying the current load and following the evolution of the voltage. This is shown in Figure 4.3. The cell was exposed to a maximum current density of 0.75 A/cm$^2$. A linear
trend in increase of cell voltage was visible. However, there was a slightly higher degradation in the first 200 hours.

Figure 4.3: The evolution of the voltage during durability under dynamic cycling conditions with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode, at 750 °C.

To comprehend the evolution of degradation, the EIS was recorded during testing at 0.625 A/cm$^2$ and 0.25 A/cm$^2$. In Figure 4.4(a) and (b), the evolution of the EIS during the durability can be seen. Since the spectra are recorded galvanostatically, both $R_s$ and $R_p$ increase during the test. Additionally, the conversion arc remains unchanged leading to an ease of analyzing EIS during testing. It is also interesting to see a rapid increase in $R_s$ in the first 200 hours in Figure 4.4(a), which can be seen as the first two curves in Figure 4.4(b). The $R_s$ change has been attributed to galvanostatic testing in Chapter-2 and is in line with the results obtained earlier. However, it is not straightforward to comprehend the change in $R_p$ under current and at the OCV due to activation of processes under current.

Following this, the ASR of the cell was calculated under current. ASR plotted is taken from the current density and the voltage values, according to the equation below:

$$\text{ASR} = \frac{OCV - V}{I}$$  \hspace{1cm} (4.1)

, where, V is the measured voltage under current, OCV is the measured open circuit voltage during the test, and I is the measured current density.

On the other hand, $R_s$ and $R_p$ are measured during impedance characterization. The contribution from $R_p$ and $R_s$ were then differentiated. This is displayed in Figure 4.5. The ASR follows the voltage trend (Figure 4.3). $R_s$ shows an increase which is in the order of 11% while $R_p$ increase is in the order of 5%. Since the magnitude of $R_s$ and $R_p$ vary significantly, the percentage of change is relative. Moreover, the plotted data
is taken from impedance spectra where a decrease in $R_p$ is seen at 5 points which correspond to increase in $R_s$ (kinks in Figure 4.3). This is the point after each cycle, where impedance spectra was obtained at 0.25 A/cm$^2$. Lowering the current density indicates a change in temperature leading to increase in $R_s$ and a change in activation of electrode processes.

The kinks in the plot result from a change in current density. At those points, the current density is approximately 0.25 A/cm$^2$, while for the rest of the plot a current density if 0.75 A/cm$^2$ is assumed. By lowering the current density, $R_s$ increases changing the mechanism of the reaction and resulting into a change in $R_p$.

i-V curves are plotted before and after the durability test to understand the extent of degradation of the cell in Figure 4.6. There is a decrease in the current density from 0.85 to 0.65 A/cm$^2$ at 1300 mV. Recalling from Figure 4.2(a), a current density of 1 A/cm$^2$ was achieved at 1300 mV. During the initial characterization, degradation of cell was observed leading to a current density of 0.85 A/cm$^2$ and an OCV decrease of 10 mV. Presence of leaks also contribute to such a behavior. However, before and after the durability test no change in OCV is observed.
Figure 4.4: The evolution of the EIS during the durability testing with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode, at 750 °C under (a)0.625 A/cm$^2$, and (b)0.25 A/cm$^2$ at the end of each cycling phase approximately 150 hours apart.
4.3 Results and Discussion

Figure 4.5: The evolution of the ASR, $R_s$, and $R_p$ during co-electrolysis with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode, at 750 °C under current.

Figure 4.6: i-V curves before and after the durability testing with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode, at 750 °C.

To analyze the contribution of electrodes, DRT analysis is performed on the cell. From the previous chapter, the DRT relaxation frequencies corresponding to Cell-
3 can be used to relate the processes since these are sister cells. In Figure 4.7(a), Nyquist plot depicts the difference in ASR where both conversion arc and electrode contribution change during the test. Since, the cell degrades during the test and galvanostatic operation leads to high overpotential, irreversible degradation may occur which is also reflected in the gas conversion impedance (arc at 1 Hz in Figure 4.7(b)). The DRT plot in 4.7(b) clearly shows an increase in high frequency response around 5 kHz, which is attributed to the fuel electrode.

![Nyquist plot](image1.png)

![DRT plot](image2.png)

**Figure 4.7:** EIS and DRT before and after the durability testing with 65% H₂O + 25% CO₂ + 10% H₂ on the fuel electrode and O₂ on the oxygen electrode, at 750 °C.

To deconvolute the degradation processes clearly, the DRT analysis is performed on EIS during the test at 0.625 A/cm² as displayed in Figure 4.8. A change in frequency response from 100-2000 Hz is seen. Under current, the arcs tend to move towards lower frequencies. Hence, a small contribution from the oxygen electrode is also present which is overshadowed by a significant increase in the fuel electrode degradation and only a single peak is observed in the DRT.
Figure 4.8: DRT during the durability testing at 0.625 A/cm² with 65% H₂O + 25% CO₂ + 10% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C.

The degradation of the cell under dynamic cycling is attributed mainly to the fuel electrode. A contribution from the oxygen electrode was also observed. Furthermore, the initial degradation of the cell and presence of leaks were also observed, which were further investigated in microstructural analysis.

4.3.1.2 Microstructural Analysis

The cell experienced high overpotential, which led to the delamination of layers. Furthermore, the pinholes leading to leaks were present from the beginning of the test and most of the cell was observed to be cracked in post-test analysis. Since the cell did not experience a change in OCV during the durability test, indication of the weakening of interfaces due to the severe testing conditions, in addition to the presence of leaks might have led to the development of cracks and delamination of the layers, were observed on cooling down the cell. In Figure 4.9, an overview of the cell with cracks is shown at the inlet of the cell. The middle and outlet part of the cell were observed to be completely oxidized on cooling leading to charging of those parts of the cell.

Figure 4.9: SEM image displaying an overview of the cell post-test.
Clearly, the initiation of the horizontal crack, highlighted in Figure 4.9, is at the oxygen electrode which thereafter spreads to the electrolyte. Since the test is galvanostatic in nature, both $R_s$ and $R_p$ increase during the course of testing. This change in $R_s$ is due to the testing as well as cracks. However, if the cracks were spread during the test, a high change in $R_s$ should have been observed [45]. Additionally, to investigate the degradation of the fuel electrode as indicated by the electrochemical testing, percolation studies were carried out at the inlet of the cell where no cracks were present. In Figure 4.10, a loss of percolation is visible close to the electrolyte in the active fuel electrode. This is also assumed to be a result of Ni migration [17], however detailed analysis was not carried out.

![Figure 4.10: Low voltage In-lens SEM image displaying the loss of percolating Nickel.](image)

To comprehend the nature of the crack, SE-2 detector was used for SEM imaging at 10 kV as shown in Figure 4.11. The nature of the cracks seem to be inter-granular, due to the weakening of interfaces as a result of high overpotential experienced by the cell. Additionally, the leaks lead to the weakening of interfaces thereby rendering parts of the cell inactive. As a result, only the active parts of the cell handle the complete overpotential leading to a faster degradation in severe cases.

![Figure 4.11: SE-2 image displaying the inter-granular cracks within the electrolyte.](image)
4.3.2 Electrochemical Analysis- Stack testing

The idea to further implement the PtG/PtL storage using dynamic wind profile was then tested on a 6-cell SOEC stack consisting of sister cells to the cell tested for dynamic test in this chapter. In this section, a comparison between the cell and the stack test is discussed owing to the difference in the current densities applied during durability testing.

In Figure 4.12, i-V comparison of the cell and the stack, prior to the durability test is plotted. A difference in OCV of 25 mV is observed between the two curves. For the stack test, the average cell voltage is plotted as a function of the current density. i-V curves seem to display similar performance. i-V and EIS curves for all the 6 cells of the stack tested under co-electrolysis conditions can be found in Manuscript-3. All the 6 cells in the stack exhibit similar performance and are tested under dynamic wind profile with a maximum current density of 0.5 A/cm$^2$. The profile was modified in order to decrease the overpotential on the cell and protect it from severe degradation, on the basis of the electrochemical analysis of the cell test performed previously.

In Figure 4.12(b), a significant difference in the EIS spectra is seen. The difference is seen in the polarization resistance and particularly in the gas conversion arc, as highlighted in the figure through the arrows. The presence of leaks in the single cell test led to a change in gas conversion which was observed as a more pronounced arc leading to increased $R_p$. For the stack test, the cells were leak tight, as observed from OCV measurements, and the conversion arc is the one for the correct gas composition. Apart from the gas-conversion arc, the $R_p$ seems comparable for the cell test than the stack test at the beginning of the test.

![Figure 4.12: i-V curves and EIS during the initial characterization with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode, at 750 °C for the cell and the stack (average cell voltage); The arrows indicate corresponding conversion arcs.](image)

The performance of the stack throughout 1000 hours of testing can be found in Manuscript-3. The plot displays that the increase in voltage is in line with the initial performance i.e., Cell-1 has the highest cell voltage, while Cell-6 has the lowest.
Although the cells show similar performance, $R_s$ was higher for Cell-1. To further understand the behavior of cell, ASR is calculated from impedance data as a summation of $R_s$ and $R_p$ in Figure 4.13. The ASR along with $R_s$ and $R_p$ for the stack only over the time span of 1000 hours of testing, can be found in Manuscript-3. In Figure 4.13, the ASR is plotted for both the cell and stack test. The first 200 hours for the stack test show higher ASR owing to a lower temperature than rest of the test. It is visible that the cell, tested for the single cell test, has significantly higher degradation and the trends are also different. This indicates that operating at higher current density leads to exposure to higher overpotentials and perhaps irreversible degradation of the cell. Furthermore, the leaks in the cell test setup also add to the overpotential. Recalling from the SEM analysis for the cell test, oxidation of parts of the cell was found post-test which indicates the presence of leaks leading to a loss of active surface area during testing.

![Figure 4.13: Comparison of the ASR evolution during the durability testing for the cell and the stack (average cell ASR).](image)

In Figure 4.14(a), i-V curves depicting the average stack cell voltage and the single cell voltage after the durability testing under co-electrolysis conditions are compared. Since the degradation of the cell is higher than the stack, this is clearly seen in the form of overlap of the two curves. For the EIS comparison in Figure 4.14(b), an increase in $R_p$ is seen for the cell (excluding the conversion arc depicted with the arrows), whereas the stack impedance does not change much from the initial. This again points to the degradation of the electrodes in the cell test.
4.3 Results and Discussion

Figure 4.14: i-V curves and EIS after the durability test with 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode, at 750 °C for cell and stack (average cell voltage); The arrows indicate corresponding conversion arcs.

To analyze the degradation, the DRT is used under current density of 0.4 A/cm$^2$. The electrode responses are similar to that of the cell test, since sister cells to the single cell test are used in the stack. In Figure 4.15, Cell-3 and Cell-5 are analyzed under current for a change in frequency response. For both the cells, an increase the DRT is found around a frequency of 1 kHz, corresponding to the fuel electrode. The increase is however, marginal. For the case of the cell test, a DRT increase of 400% is found for the fuel electrode while for the stack test, the DRT increase is in the order of 25%, indicating a significantly lower degradation. Following this, overpotential of the cells of the stack before and after the test are calculated according to the following equation:

$$Op = V - OCV - IR_s$$ (4.2)

In Chapter 2, the overpotential calculation did not exclude $R_s$ due to different testing modes. However, here a comparison is drawn under similar conditions and exclusion of $R_s$ can be justified. The values of the overpotential are in the order of 100-110 mV. Since the stack was operated at a lower current density, severe degradation was avoided. Ni migration and therefore the loss of percolation has been previously observed under high overpotentials experienced by the fuel electrode [16]. This is expected to be the case for the cell test, where the leaks end up stressing the cell furthermore.

Additionally, the stack was aimed at production of H$_2$ and syngas. In Manuscript-3, the power density and H$_2$ production are plotted as a function of time. Both the curves follow the current density trend such that syngas is being produced throughout the test, on a reasonably constant rate. The total syngas production was in the order of 3000 moles during 1000 hours of testing under the simulated wind profile. An increase in the current density would increase the H$_2$ and syngas production, however degrading the cells.
4.4 Conclusions

Fuel electrode supported cell and stack were tested under dynamic load conditions aimed at energy storage. For the cell test, the current density led to a high overpotential on the cell along with the leaks from the start of the test leading to degradation of the cell. The electrochemical analysis suggest the fuel electrode degradation as the major contributor. From the SEM analysis, cracks and delamination of layers are also indicated post test due to weakening of interfaces during testing. Following this, the stack was tested under lower current densities which led to only marginal degradation of the cells in the stack. The degradation was also attributed to the fuel electrode. During the stack test, limiting the current density led to lowering the voltage degradation from 15%/1000 h to 0.8%/1000 h. The stack test led to a consistent performance with the leak tightness leading to constant H$_2$ and syngas production which serves as a candidate for energy storage in real case scenario.
CHAPTER 5

Leak analysis in the cell tests performed under steam and co-electrolysis: Effect of pinholes and setup

5.1 Introduction

In the previous chapters, the need for electrode modifications along with different operating modes aimed at energy storage have been elaborated. The degradation of both the electrodes of the SOECs was observed through the electrochemical analysis. Additionally, SEM analysis revealed cracks in the electrolyte. The presence of leaks was also indicated which may lead to local combustion, changing the temperature of the cell leading to the lowering of OCV. In the tests performed in this work, a high steam content was maintained with only 10% H₂. While accounting for the OCV, this gas composition is particularly sensitive to the leaks which is evident even with a small fraction of change in gas composition i.e., due to the calculation of Nernst potential, a change in gas conversion is more susceptible and visible at a high steam content and respectively low hydrogen content [46]. Furthermore, the leaks can lead to higher overpotential than desired. Leaks lead to a lower OCV, forcing the cell to work under higher current densities to achieve the desired voltage. This has also been indicated in the previous chapters as a contributor to degradation of the cells tested for durability as discussed in Manuscript-2. Here, the data analysis was performed on the cells tested during this PhD as well as from the data recorded over the last 10 years to gain a quantitative understanding of the origin and the propagation of pathways leading to the degradation of cells. In this chapter, the cells were analyzed under a high steam content (80-90% steam) and co-electrolysis conditions to account for the leaks through a prominent change in the gas conversion arc. The cells were, moreover, analyzed for gas diffusion and crossover. The electrochemical analysis at ambient and high pressure conditions were compared. Based on the diffusion, modeling was performed along with post-test SEM analysis.
5.2 Experimental

Five different types of fuel electrode supported cells were analyzed for leaks as listed below:

- **Cell type-A-** Ni-YSZ fuel electrode, YSZ electrolyte, lanthanum strontium manganite (LSM)-YSZ oxygen electrode, LSM contact layer
- **Cell type-B-** Ni-YSZ fuel electrode, YSZ electrolyte, LSC-CGO oxygen electrode, LSM contact layer
- **Cell type-C-** Ni-YSZ fuel electrode, YSZ electrolyte, CGO barrier layer, LSCF-CGO oxygen electrode
- **Cell type-D-** Ni-YSZ fuel electrode, YSZ electrolyte, CGO barrier layer, LSC-CGO oxygen electrode
- **Cell type-E-** Ni-YSZ fuel electrode (optimized particle size distribution as compared to Cell-D), YSZ electrolyte, CGO barrier layer, LSC-CGO oxygen electrode

All the tests were carried out at ambient pressure in the cell test setup described in literature [32, 33]. The active cell area is 16 cm². Reduction of cell was performed according to the procedure reported in literature [16].

A standardized electrochemical characterization of the cells was performed at 850 °C, 800 °C, 750 °C, 700 °C and 650 °C, depending on the aim of the test. i-V and EIS measurements were performed with air or O₂ on the oxygen electrode, and with 4%, 20%, 50%, 80% or 90% steam in H₂ on the fuel electrode. Additionally, characterization in co-electrolysis gas mixture was carried out for some of the cells with 45% H₂O + 45% CO₂ + 10% H₂ and 65% H₂O + 25% CO₂ + 10% H₂ being supplied to the fuel electrode.

The EIS measurements were carried out under open circuit voltage (OCV) condition, using a Solartron frequency analyzer and an external shunt resistor in series with the cell as described in previous chapters. EIS data analysis was performed using the software Ravdav [34].

After cooling down the cells, the post-test SEM analysis was performed with a Supra-35 scanning electron microscope (SEM) equipped with a field emission gun (FE-SEM, Carl Zeiss) and an energy-dispersive X-ray spectrometer (EDX, Thermo Electron Corporation). The cells were embedded in epoxy and carbon coated to avoid charging of the sample surface and to ensure a grounded connection. The images were taken at 10 and 5 kV. Backscatter and Secondary electron (SE-2) detectors were used for imaging.
5.3 Results and Discussion

5.3.1 Electrochemical Analysis

As aforementioned, the need for the leak analysis arose due to the prominent effect of leaks visible at high steam concentrations as a part of polarization resistance. In this context, characterization of the cells is of essence in order to identify the response of fuel and oxygen electrodes. In Figure 5.1(a), EIS for Cell type-E tested under co-electrolysis conditions with 65% H\textsubscript{2}O + 25% CO\textsubscript{2} + 10% H\textsubscript{2} on the fuel electrode with oxygen and air on the oxygen electrode is compared. For the EIS under oxygen, the resistance is higher. Similarly, in Figure 5.1(b), EIS for Cell type-B tested under co-electrolysis conditions with 45% H\textsubscript{2}O + 45% CO\textsubscript{2} + 10% H\textsubscript{2} on the fuel electrode, and oxygen and air on the oxygen electrode, is compared. EIS, in this case as well, is higher with oxygen on the oxygen electrode. Since the oxygen content in air as only 21% of the total flow, the resistance should be lower or almost similar in oxygen to that in air, under the same fuel electrode gas composition.

![Graph a](image1.png)

![Graph b](image2.png)

**Figure 5.1:** Gas shift analysis on the oxygen electrode under co-electrolysis conditions (a) Cell type-E with 65% H\textsubscript{2}O + 25% CO\textsubscript{2} + 10% H\textsubscript{2} on the fuel electrode, (b) Cell type-B with 45% H\textsubscript{2}O + 45% CO\textsubscript{2} + 10% H\textsubscript{2} on the fuel electrode at 750 °C.
Since the change in the resistance is seen in the form of a low frequency arc in the EIS, the frequency of process(es) contributing to this were investigated next. For this purpose, the distribution of relaxation times (DRT) analysis was utilized \cite{47} and the resulting plots are displayed in Figure 5.2. Gas shift DRT analysis was performed wherein, by changing gas composition on one electrode while keeping the gas at the other electrode constant, a frequency response for the individual electrodes can be separated. In Figure 5.2, a shift from O\textsubscript{2} to air for Cell type-E and Cell type-B are displayed such that a visible change in the response is observed at 1 Hz. The frequency of approximately 1 Hz is assigned to the gas concentration resistance in literature \cite{12}. It is interesting to note that the gas concentration resistance is higher under O\textsubscript{2} than in air, which indicates the leaks leading to change in the gas composition to a greater extent in pure oxygen than in air. This implies that if oxygen is leaking to the fuel side through a pinhole, for instance, it can react with H\textsubscript{2} to form H\textsubscript{2}O thereby changing the ratio of H\textsubscript{2} present visible in the form of the gas concentration impedance.

![Figure 5.2: DRT analysis with a shift from oxygen to air on the oxygen electrode under co-electrolysis conditions (a) Cell type-E with 65% H\textsubscript{2}O + 25% CO\textsubscript{2} + 10% H\textsubscript{2} on the fuel electrode, (b) Cell type-B with 45% H\textsubscript{2}O + 45% CO\textsubscript{2} + 10% H\textsubscript{2} on the fuel electrode at 750 °C.](image)

Different kinds of leaks while testing a cell in the setup described in the experimental section have previously been reported \cite{48}. Internal leaks were attributed to diffusion of gases through pinhole, which were investigated in this PhD. External leaks through the sealing has also been previously reported. In addition, ionic leaks may also be present which are difficult to identify. One way would be to draw an i-V curve under electrolysis conditions in dry H\textsubscript{2} gas to ensure the ionic leak content. This led to the analysis of origin and propagation of leaks. The case of gas diffusion
was considered such that the gas leaking only through the pinholes are considered. This implies the diffusion of $O_2$ from the oxygen electrode to fuel electrode, and the diffusion of $H_2$ from fuel electrode to oxygen electrode leading to the modification of the ratio of steam to $H_2$ in the fuel electrode. The leaks due to only diffusion, either of $O_2$ or of $H_2$ gas or both simultaneously are considered. An illustration of leak through a pinhole by diffusion is displayed in Figure 5.3.

![Illustration of the diffusion of gas through a pinhole through the electrodes and electrolyte for diffusion.](image)

**Figure 5.3:** Illustration of the diffusion of gas through a pinhole through the electrodes and electrolyte for diffusion.

To analyze the data for five different cell types based on pure diffusion, the change in OCV was calculated such that:

$$\Delta OCV = OCV_{Nernst} - OCV_{measured} \quad (5.1)$$

wherein, $OCV_{Nernst}$ for steam electrolysis is thermodynamically calculated as:

$$E = E_0 + \frac{RT}{2F} \ln \frac{P_{H_2O}^{in}}{P_{H2}^{in} \sqrt{P_{O2}^{in}}} \quad (5.2)$$

For $CO_2$ electrolysis, the equation is as follows:

$$E = E_0 + \frac{RT}{2F} \ln \frac{P_{CO_2}^{in}}{P_{CO}^{in} \sqrt{P_{O2}^{in}}} \quad (5.3)$$

where, $E_0$ is the standard Nernst potential at a given temperature, $R$ is the universal gas constant, $T$ is the temperature, $F$ is the Faraday’s constant, and $P_{H2O}$, $P_{H2}$, $P_{CO_2}$, $P_{CO}$ and $P_{O2}$ are the partial pressures of the components taking part in the reaction. For co-electrolysis where both steam and $CO_2$ are being electrolyzed simultaneously, the ratio of inlet equilibrium is used to calculate the overall Nernst potential.
Change in the OCV is calculated for both oxygen and air cases, keeping the fuel composition constant. Moreover, difference between the OCV values in air and oxygen, as measured is calculated as:

\[ \Delta OCV_{sub} = \Delta OCV_{O_2} - \Delta OCV_{Air} \]  \hspace{1cm} (5.4)

where, \( \Delta OCV_{sub} \) is a measure of a difference in the air and oxygen OCVs which will be utilized to calculate the leak.

When only \( H_2 \) is diffusing through the pinhole implying a pure hydrogen leak, an equal amount of leak would be observed in both air and oxygen. On the other hand, if only \( O_2 \) is diffusing through the pinhole in the case of a pure oxygen leak, diffusion is dependent on the partial pressure of the oxygen content. For air, the diffusion will be 0.21 times that of oxygen. For a pure oxygen leak, the change in OCV differences is calculated as follows:

\[ \Delta OCV_{diff} = (\Delta OCV_{O_2} - \Delta OCV_{Air}) - (\Delta OCV_{O_2,new} - \Delta OCV_{Air}) \]  \hspace{1cm} (5.5)

where, \( OCV_{O_2,new} \) is the calculated OCV in \( O_2 \) assuming pure \( O_2 \) leak, based on the \( OCV_{Air,measured} \).

\( \Delta OCV_{diff} \) is the deviation from the change in the theoretical value when assuming a pure oxygen leak based on the fact that the OCV measured in air is only due to the oxygen leak.

Considering the equations, the values were calculated as displayed in Table 5.1. The data set displayed no pattern and exhibited a scatter plot which leads to the possibility of both \( H_2 \) and \( O_2 \) diffusing through the pinhole simultaneously. The empty value in the table represent the cases where a pure oxygen diffusion will lead to excessive leak, making them invalid. In Table 5.1, Cell type-A with A1, A2 and A3 depicts the cells of the same cell type tested under different conditions.
To analyze the nature of the leaks, the equivalent leak currents are calculated as follows:

\[
\text{Number of moles} = \frac{\text{Excess } O_2 (L/h)}{22.4 \text{ L/mol}} \tag{5.6}
\]

\[
\text{Leak current} = \frac{\text{Number of moles} (mol/h) * F (A \text{ s/mol}) * 4}{3600 \text{ } \times \text{16 cm}^2} \tag{5.7}
\]

where, F is the Faraday constant, and 4 refers to the number of electrons per mole of excess $O_2$ gas.

The leak currents further help to understand the case of pure $H_2$ and $O_2$ leaks. For the case of co-electrolysis and steam electrolysis with 80-90% steam in the fuel gas composition, leak currents with $O_2$ and air on the oxygen electrode are plotted in Figure 5.4. In this figure, two trends line are shown, wherein Trend1 is depicting the case of pure hydrogen leak while Trend 2 is depicting the case of pure oxygen leak. Furthermore, 50% $H_2O + 50% H_2$ fuel gas composition is considered to comprehend the nature of leaks, while changing the gas on the oxygen electrode from $O_2$ to air and plotted as leak current in air vs $O_2$ in Figure 5.5. The values for the leak currents thus obtained, are presented in Table 5.2. The empty values are due to the incomplete data availability or inaccuracy of the testing conditions, which are therefore disregarded. These values are taken as 0 in Figure 5.5. For the case of a pure $H_2$ leak, equal leak currents should be obtained with $O_2$ and air, as seen for Cell type-A in Figure 5.4. However, in Figure 5.5 this theory is inconsistent. Additionally, for the case of pure $O_2$ leak the ratio between leak currents should be related to the partial pressure of the $O_2$ present. The leak is significantly lower and there is no clear correlation. As

### Table 5.1: Change in the OCV for different cell types.

<table>
<thead>
<tr>
<th>Cell type</th>
<th>Fuel electrode composition</th>
<th>$\Delta OCV_{O_2}$ (mV)</th>
<th>$\Delta OCV_{air}$ (mV)</th>
<th>$\Delta OCV_{sub}$ (mV)</th>
<th>$\Delta OCV_{diff}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>45%CO$_2$+45%H$_2$O+10%H$_2$</td>
<td>12.5</td>
<td>9.4</td>
<td>3.1</td>
<td>-</td>
</tr>
<tr>
<td>A2</td>
<td>45%CO$_2$+45%H$_2$O+10%H$_2$</td>
<td>14.7</td>
<td>10.9</td>
<td>3.8</td>
<td>85.4</td>
</tr>
<tr>
<td>A3</td>
<td>45%CO$_2$+45%H$_2$O+10%H$_2$</td>
<td>106.7</td>
<td>119.4</td>
<td>-12.7</td>
<td>83.4</td>
</tr>
<tr>
<td>B1</td>
<td>80%H$_2$O+20%H$_2$</td>
<td>29.5</td>
<td>20.5</td>
<td>8.9</td>
<td>-</td>
</tr>
<tr>
<td>B2</td>
<td>80%H$_2$O+20%H$_2$</td>
<td>10.3</td>
<td>9.1</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>B3</td>
<td>80%H$_2$O+20%H$_2$</td>
<td>16.4</td>
<td>11.1</td>
<td>5.3</td>
<td>19.9</td>
</tr>
<tr>
<td>B4</td>
<td>80%H$_2$O+20%H$_2$</td>
<td>28.6</td>
<td>19.1</td>
<td>9.5</td>
<td>17.9</td>
</tr>
<tr>
<td>C1</td>
<td>45%CO$_2$+45%H$_2$O+10%H$_2$</td>
<td>9.9</td>
<td>8.1</td>
<td>1.8</td>
<td>106.6</td>
</tr>
<tr>
<td>C2</td>
<td>45%CO$_2$+45%H$_2$O+10%H$_2$</td>
<td>23.6</td>
<td>14.6</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>45%CO$_2$+45%H$_2$O+10%H$_2$</td>
<td>9.6</td>
<td>6.7</td>
<td>2.9</td>
<td>55.2</td>
</tr>
<tr>
<td>C4</td>
<td>45%CO$_2$+45%H$_2$O+10%H$_2$</td>
<td>11</td>
<td>7.6</td>
<td>3.4</td>
<td>84.3</td>
</tr>
<tr>
<td>C5</td>
<td>45%CO$_2$+45%H$_2$O+10%H$_2$</td>
<td>19.8</td>
<td>13.4</td>
<td>6.3</td>
<td>107.1</td>
</tr>
<tr>
<td>D1</td>
<td>90%H$_2$O+10%H$_2$</td>
<td>12.9</td>
<td>4.5</td>
<td>8.4</td>
<td>-</td>
</tr>
<tr>
<td>E1</td>
<td>25%CO$_2$+65%H$_2$O+10%H$_2$</td>
<td>29.1</td>
<td>7.7</td>
<td>21.4</td>
<td>-</td>
</tr>
</tbody>
</table>
a result, the leaks are due to both H₂ and O₂ diffusion. Furthermore, the higher the flow, the higher is the leak, which might be due to convection, with increase in gas crossover at higher flow rates. For Figure 5.4, a total flow rate of 12 NmlPm of gas flow was used on the fuel electrode while for Figure 5.5, the tests were carried out with 25 NmlPm of gas flow on the fuel electrode. Hence, the leaks are dependent on both diffusion and flow. Reconsidering Figure 5.3, simultaneous gas diffusion through the pinholes seems highly probable.
Figure 5.4: Leak current in air vs. leak current in oxygen for all the cells analyzed under co-electrolysis and steam electrolysis conditions (with 80% and 90% steam in the fuel electrode) with 12 NL/h minimum flow; Trend1: H₂ leak, Trend2: O₂ leak.
Figure 5.5: Leak current in air vs. leak current in oxygen for all the cells analyzed with 50% H₂O + 50% H₂ on the fuel electrode with 24 NL/min minimum flow; Trend1: H₂ leak, Trend2: O₂ leak.
To further understand the diffusion through the pinholes, diffusion coefficients are calculated for binary and multicomponent mixtures based on Knudsen, Binary and Stefan-Maxwell diffusion models. From the Kinetic Theory of Gases, Knudsen diffusion coefficient is calculated as:

$$D_{i,K}^{eff} = \frac{\epsilon \rho_p}{\tau} \sqrt{\frac{8RT}{\pi M_i}}$$  \hspace{1cm} (5.8)$$

where, $M_i$ is the molecular weight of component $i$, $\rho_p$ is the pore diameter, $\epsilon$ is the electrode porosity and $\tau$ is the electrode tortuosity.

To calculate the Binary diffusion coefficient, Chapman-Enskog correlation is used as
follows:

\[ D_{i,j}^{\text{eff}} = \frac{\epsilon}{\tau} D_{i,j} = \frac{\epsilon}{\tau} 0.001858 T^{1.5} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{0.5} \left( \frac{p\sigma_{i,j}^2}{\Omega_D} \right) \]  

(5.9)

where, \( T \) is the temperature, \( M_i \) and \( M_j \) are molecular weights of species \( i \) and \( j \), \( p \) is the pressure, \( \sigma_{i,j} \) is the average collision diameter between the species \( i \) and \( j \) and \( \Omega_D \) is the dimensionless collision integral calculated using Lennard-Jones model. \( \sigma \) and \( \Omega \) values are taken from literature [49, 50]. The values of \( \epsilon \) and \( \tau \) are taken from reported values in literature [51].

For the calculation of diffusion in multicomponent mixtures, Stefan-Maxwell diffusion coefficient is calculated as follows:

\[ D_{SM} = \sum \frac{1 - y_i}{y_j + y_k} D_{ij} + \frac{y_k}{y_j} D_{ik} \]  

(5.10)

where, \( y \) represents the mole fraction of species and \( D \) is the binary diffusion coefficient calculated in the previous equation.

Based on the calculated diffusion coefficients and molar fractions, the case of hydrogen combustion with \( O_2 \) to form steam is considered according to the following equation:

\[ H_{2,\text{flow,measured}} = H_{2,\text{flow, theoretical}} - aD_{H_2} \chi_{H_2} - 2aD_{O_2} \chi_{O_2} \]  

(5.11)

where, \( a \) is the variable which will be calculated for each test which is analyzed to find a correlation between leaks and diffusion.

The calculated \( a \) values for the case of oxygen and air on the oxygen electrode is displayed in Figure 5.6. Here, \( \chi_{O_2} \) is 1 for oxygen and 0.21 for air and \( \chi_{H_2} \) is 0.1 or 0.2 depending on the test. The line with slope = 1 depicts pure diffusion scenario. It should be the values of \( a \) for Cell type-A lie on the pure diffusion line and hence are not visible on the plot, since this is the case of co-electrolysis. A good scatter in the data acquired is evident which indicates simultaneous diffusion of both hydrogen and oxygen, but there are other factors influencing leaks as well.
It was of further interest to analyze the data, not only under ambient pressure cell tests, but also under pressurized conditions. Previously at DTU, steam electrolysis has been successfully carried out on a pressurized setup as can be found in literature.
The authors tested fuel electrode supported cell under 50% H$_2$O + 50% H$_2$ on the fuel electrode and air on the oxygen electrode. The pressure dependency of leak current is displayed in Figure 5.7.

**Figure 5.7:** Leak current vs. pressure for a stack tested at 50% H$_2$O + 50% H$_2$ on the fuel electrode and air on the oxygen electrode.
This led to the investigation of the pressure dependency of the leaks. During the pressure test, two different types of leaks may be encountered namely:

- A pressure independent Stefan-Maxwell diffusion leak
- A pressure dependent Knudsen leak

Considering diffusion in the multicomponent mixtures, Maxwell diffusion and Knudsen diffusion are taking place simultaneously in the pressurized system. The total diffusion constant under pressurized conditions is determined according to the following equation:

\[
\frac{1}{D_{total}} = \frac{1}{D_{SM}} + \frac{1}{D_{k}} = \frac{P}{D_{SM}^0} + \frac{1}{D_{k}}
\]  

(5.12)

where, \(D_{SM}\) and \(D_{k}\) are the previously calculated stefan-maxwell and knudsen diffusion coefficients, respectively. \(D_{SM}\) is dependent inversely on pressure and this is represented by pressured independent term \(D_{SM}^0\), while \(D_{k}\) is independent of pressure.

Additionally, to calculate the rate of diffusion under pressure, the following equation is used:

\[
J = D_{total} \nabla C = D_{total} \nabla C^0 P
\]  

(5.13)

According to these equations, for the rate of diffusion calculation, pressure terms cancel out for the case of Stefan-Maxwell diffusion making it pressure independent, while the Knudsen diffusion rate is proportional to the pressure. To fit the data in Figure 5.7, an accurate contribution from Stefan-Maxwell and Knudsen diffusion needs to be found out using coefficients, which has not been performed.

5.3.2 Microstructural Analysis

Electrochemical data analysis indicate the presence of significant amount of leaks in all the cell tests analyzed in this chapter. The leaks can be attributed to both diffusion and the flow of gases crossing over. To substantiate the hypothesis, the post-test SEM images of some of the tests are displayed in Figure 5.8 with different layers labeled in the figure.

Leaks are usually encountered in the form of cracks (vertical) and/or delamination of layers and/or grain boundary weakening leading to cracks in the electrolytes. In Figure 5.8(a) and(b), backscatter images of the cells with cracks in the electrolyte are presented while Figure 5.8(c) was taken using SE-2 detector. In Figure 5.8(a), the grain boundary crack is visible leading to the leaks in the cell. This indicates weakening of the cell due to testing. In Figure 5.8(b), a magnified image shows the pinholes present in the cell through which diffusion of hydrogen and oxygen are taking place. Figure 5.8(c) presents the extreme case of cracks formed in the cell during testing. The cracks goes all the way through the electrolyte to the fuel electrode. This leads to an increase in leaks and propagation rendering parts of the cell inactive.
5.4 Conclusions

The analyzed test data and SEM indicate the cause of cracks to be pinhole diffusion as well as gas crossover due to difference in flow and partial pressure.

![Figure 5.8: SEM images displaying pinholes and cracks in the tested cells for Cell type-E, (a) grain boundary crack in the electrolyte-backscatter detector, (b) pinholes in the electrolyte-backscatter detector, and (c) cracks in the fuel electrode through the electrolyte-SE-2 detector.](image)

5.4 Conclusions

In this chapter, a comprehensive analysis of origin and propagation of leaks for cells tested under co-electrolysis and steam electrolysis with 80-90% steam on the fuel electrode is performed. The leaks were indicated to be a combination of both hydrogen and oxygen gas diffusion. In addition, a flow dependency of the leaks was also indicated implying an increase in gas crossover at higher flow rates. Furthermore, for the case of pressurized system, the overall diffusion coefficient was also modeled for such a case. To substantiate the leaks, post-test SEM analysis revealed grain boundary cracks, cracks and pinholes in the tested cell.

To avoid the leaks through pinholes, a robust gas shift analysis during initial characterization would be useful. Additionally, a cell which is only reduced and not tested could be analyzed under SEM for analyzing the amount of pinholes. This could serve as a reference. Carrying out i-V for the identification of ionic leaks could also be of an advantage to narrow down the origin of leaks. To protect the cell from propagation of leaks, a lower current density and lower steam content (approximately 50%) would be advisable for durability testing.
CHAPTER 6

High pressure testing

6.1 Introduction

In the Power-to-Liquid/Power-to-Gas scenarios aimed at syngas and methane production, pressurized testing is beneficial. The production of methane through Fischer-Tropsch is favoured at pressures of 10-100 bar [13, 53]. Furthermore, the transport of fuels is usually performed under pressure [5]. It has been previously reported through modeling that testing the SOECs under pressurized conditions can lead to internal methane formation [54]. On these lines, a test on a stack was previously carried out at DTU to demonstrate the methane formation, wherein approximately 21% of methane was observed on dry gas basis in the fuel outlet [25].

In this work, the cell type with improved performance, tested for dynamic conditions, was also tested under pressurized conditions. Due to the setup limitations, only steam electrolysis studies could be performed. In this work, a SOEC is tested under steam electrolysis for initial characterization at 1, 3, 5 and 10 bars at 750 °C. A comparison between the resistances under pressurized conditions is briefly discussed along with extent of leaks during testing. Evolution of the reaction mechanisms is briefly discussed.

6.2 Experimental

The experimental setup has been previously described elsewhere [55]. The cell was pressurized in the autoclave with the use of pressure controllers as depicted in Figure 6.1. The gases are fed to the electrode by mass flow controllers, such that the pressure in the autoclave and the electrodes of SOEC was the same due to piping which is open to the autoclave interior. Safety measures related to over-pressure or leaks were accounted for through the pressure sensors. An active balance of pressure was engaged through a proportional-integral-derivative (PID) loop.
Figure 6.1: Schematic of the pressure control in the cell test setup as previously described in [55].

The cell consists of LSC-CGO oxygen electrode with CGO barrier layer, YSZ electrolyte, Ni-YSZ active fuel electrode and support. Ni-YSZ structure ratio has been optimized in terms of porosity and particle size distribution [16]. The cells were tested in the schematic of the test house as described in literature [55]. To ensure electrical contact, alumina pieces are pressed together between the cell, the gas distribution layers and the current collectors, while the the gases are passed to the electrodes through the has channels in the cell test holder. The gas channels allow the gas diffusion to the SOEC electrodes and a cross-flow is maintained through the gas distribution layers. On the oxygen electrode, a 0.2 mm thick gold foil is used for current collection while on the fuel electrode a 0.2mm thick Ni plate and Ni meshes are used as described in [32]. To establish a good electrical contact between the cell components, 8 kg of weight was placed on the top of the cell. The cell was reduced at 850 °C with 5% H₂ and 95% N₂ being fed to the fuel electrode, and air on the oxygen electrode for 2 hours. Thereafter, the characterization was carried out at 750 °C. During the characterization, gas mixtures of 20% H₂O + 80% H₂, 50% H₂O + 50% H₂, 80% H₂O + 20% H₂ and 90% H₂O + 10% H₂ were fed to the fuel electrode with either air or O₂ on the oxygen electrode. The characterization was carried out at 1, 3, 5 and 10 bars with the gas mixtures described above. i-V curves were drawn with limits of 700 and 1300 mV in FC and EC mode, respectively. For the electrochemical impedance measurement, Solartron 1255 frequency analyzer with an external shunt resistor in series with the cell at zero DC current was used. The spectra were recorded with 12 points per decade in a frequency range of 96850 to 0.08 Hz. The cell test house was short-circuited and the impedance was used for correction of the impedance obtained. The ohmic resistance (R_s) was taken as the real part of the spectra at 96850 Hz, while the polarization resistance (R_p) was obtained by subtracting the real part of the spectra between 96850 and 0.08 Hz. All the spectra were taken at OCV.
6.3 Results and Discussion

6.3.1 Characterization at various pressures

The cell was characterized at 750 °C at 1 bar, thereafter gradually increasing the pressure to 3, 5, 8 and 10 bars. The i-V curves are plotted for the test in Figure 6.2. The OCV increases with increase in pressure, which is in line with the thermodynamic calculations. Furthermore, the performance in the EC mode improves with the increase in pressure. On the other hand, for the FC mode the improvement is seen only up to 5 bars, after which the performance gets worse. To analyze this, the measured OCV values are compared to the theoretical ones in Table 6.1.

![Figure 6.2: i-V curves under pressurized conditions with 50% H₂O + 50% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C.](image)

At OCV, the impedance spectra are measured and displayed in Figure 6.2. It is interesting to see an increase in $R_s$ with pressure. The $R_p$ decreases with an increase in pressure. The values are displayed in the Table 6.2. Temperature variations are also considered to account for the $R_s$ change.

To account for the inconsistency in the FC and EC modes, OCV difference is correlated with the presence of leaks. Additionally, the change in $R_s$ could also be explained by temperature variation due to leaks.
6.3 Results and Discussion

Figure 6.3: EIS under pressurized conditions with 50% H₂O + 50% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C under OCV.

Table 6.1: OCV calculations with 50% H₂O + 50% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>OCV\text{theoretical} (V)</th>
<th>OCV\text{measured} (V)</th>
<th>ΔOCV (mV)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.996</td>
<td>0.983</td>
<td>13</td>
<td>761</td>
</tr>
<tr>
<td>3</td>
<td>1.016</td>
<td>1.012</td>
<td>4</td>
<td>749</td>
</tr>
<tr>
<td>5</td>
<td>1.027</td>
<td>1.021</td>
<td>6</td>
<td>755</td>
</tr>
<tr>
<td>8</td>
<td>1.038</td>
<td>1.024</td>
<td>14</td>
<td>749</td>
</tr>
<tr>
<td>10</td>
<td>1.043</td>
<td>1.028</td>
<td>15</td>
<td>750</td>
</tr>
</tbody>
</table>

Table 6.2: ASR calculations with 50% H₂O + 50% H₂ on the fuel electrode and O₂ on the oxygen electrode at 750 °C.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>R_s\text{measured} (Ω cm²)</th>
<th>R_p\text{measured} (Ω cm²)</th>
<th>ASR\text{EIS} (Ω cm²)</th>
<th>ASR_{i-V} (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.124</td>
<td>0.106</td>
<td>0.23</td>
<td>0.234</td>
</tr>
<tr>
<td>3</td>
<td>0.158</td>
<td>0.099</td>
<td>0.257</td>
<td>0.276</td>
</tr>
<tr>
<td>5</td>
<td>0.153</td>
<td>0.089</td>
<td>0.242</td>
<td>0.258</td>
</tr>
<tr>
<td>8</td>
<td>0.189</td>
<td>0.1</td>
<td>0.289</td>
<td>0.302</td>
</tr>
<tr>
<td>10</td>
<td>0.196</td>
<td>0.115</td>
<td>0.31</td>
<td>0.314</td>
</tr>
</tbody>
</table>

From Table 6.1 and 6.2, the change in the behavior of the cell while increasing pressure from 5 to 8 bars is visible. A decrease in OCV is observed leading to temperature variations, which in part can explain the increase in R_s. Interestingly, R_p seems
to increase at 8 bar from 5 bar, which can be accounted for by the presence of leaks causing the change in gas conversion. This is further discussed through impedance analysis.

6.3.2 Impedance analysis

To analyze the dependency of polarization resistances with pressure along with identification electrode response, DRT analysis was performed [47]. By varying the fuel electrode gas composition, while keeping the gas composition unchanged on the oxygen electrode, the characteristic frequencies of the fuel electrode processes are identified. Similarly, by varying the oxygen electrode gas from O$_2$ to air while keeping the fuel electrode gas composition constant, characteristic frequencies for the processes related to the oxygen electrode are identified. The frequencies corresponding to the electrodes are listed in Table 6.3. Additionally, Figure 6.4 displays the response of the individual electrodes for the analysis is performed on the spectra obtained at 1 bar.

![Figure 6.4: DRT analysis for the identification of the electrode response for (a) the fuel electrode, and (b) the oxygen electrode, at 750 °C and 1 bar.](image)
Table 6.3: DRT analysis for the identification of characteristic frequencies of the electrodes at 1 bar.

<table>
<thead>
<tr>
<th>Process</th>
<th>Relaxation frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Gas conversion</td>
<td>1-3 Hz</td>
</tr>
<tr>
<td>2 Diffusion</td>
<td>30-50 Hz</td>
</tr>
<tr>
<td>3 Oxygen electrode</td>
<td>100-200 Hz</td>
</tr>
<tr>
<td>4 Fuel electrode, TPB processes</td>
<td>1-2 kHz</td>
</tr>
<tr>
<td>5 Fuel electrode, oxygen ion transport</td>
<td>8-10 kHz</td>
</tr>
</tbody>
</table>

Once the electrode responses are identified, the aim was to analyze the effect of pressure on the frequency response. Firstly, a bode plot corresponding to the Nyquist plot in Figure 6.3 is displayed. Additionally, in Figure 6.6, DRT plot is displayed under 50% H$_2$O + 50% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode conditions, at 750 °C.

Figure 6.5: Bode plot under pressurized conditions with 50% H$_2$O + 50% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.
6.3 Results and Discussion

Figure 6.6: DRT under pressurized conditions with 50% H$_2$O + 50% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

Previously, it has been reported that an increase in pressure leads to a decrease in the summit frequency for the low frequency arc (gas conversion) and increase in the summit frequency for the high frequency arc (TPB reactions) [55]. In Figure 6.5, this is clearly seen. However, it should be noted that increase in pressure generally leads to a decrease in $R_p$. The $R_p$ change is reflected in the high frequency arcs, since the gas conversion is independent of pressure and depends only on the concentration of reactants. Additionally, the DRT plot is noisy in the low frequency region, however, the frequency trends are similar to the ones reported in literature [55] and following this, fitting of the EIS data is performed.

To analyze the impedance spectra shown in Figure 6.3, data fitting is performed with an equivalent circuit with an inductance (L), serial resistance (R), 2 R-Q elements for fuel electrode reactions, Gerischer (G) for oxygen electrode reaction, and 2 R-Q elements for gas diffusion and conversion, connected in series. A schematic of the equivalent circuit is shown in Figure 6.7. Here, R0 denotes the ohmic resistance with L as the inductance. R1-Q1 is the gas conversion circuit which is basically modeled in a way to resemble an RC circuit. Gas diffusion is modeled as R2-Q2. G is the Gerischer element used for oxygen electrode process, while the fuel electrode processes are modeled using R3-Q3 and R4-Q4. This is a standard equivalent circuit used for solid oxide cell modeling in literature [20, 56]. Furthermore, previously Hauch et.al have tested similar cells under ambient pressure using the same circuit model [57]. The fitted values for resistances are displayed in Table 6.4. The error in fitting values is in the order of $10^{-8}$-$10^{-9}$ in terms of $\chi^2$.

Figure 6.7: Schematic of an equivalent circuit used for the impedance data fitting.
Table 6.4: Impedance fitting: elements of the equivalent circuit, R in Ωcm², fs in Hz.

<table>
<thead>
<tr>
<th>P</th>
<th>R0</th>
<th>R1</th>
<th>fs1</th>
<th>R2</th>
<th>fs2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>fs5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.12</td>
<td>0.053</td>
<td>7570</td>
<td>0.016</td>
<td>2332</td>
<td>0.011</td>
<td>1E-10</td>
<td>0.032</td>
<td>4.09</td>
</tr>
<tr>
<td>3</td>
<td>0.154</td>
<td>0.047</td>
<td>11891</td>
<td>0.016</td>
<td>4712</td>
<td>0.006</td>
<td>1E-10</td>
<td>0.033</td>
<td>1.36</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
<td>0.04</td>
<td>13991</td>
<td>0.016</td>
<td>6968</td>
<td>0.003</td>
<td>0.008</td>
<td>0.03</td>
<td>0.78</td>
</tr>
<tr>
<td>8</td>
<td>0.186</td>
<td>0.05</td>
<td>12499</td>
<td>0.016</td>
<td>4685</td>
<td>0.006</td>
<td>1E-10</td>
<td>0.038</td>
<td>0.47</td>
</tr>
<tr>
<td>10</td>
<td>0.192</td>
<td>0.06</td>
<td>10846</td>
<td>0.016</td>
<td>3279</td>
<td>0.005</td>
<td>1E-10</td>
<td>0.038</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Note: The values of R2 and R4 remain unchanged and are not considered reliable.

To verify the fit of the spectra, the impedance spectra with 20% H₂O + 80% H₂ on the fuel electrode and O₂ on the oxygen electrode, and 50% H₂O + 50% H₂ on the fuel electrode and air on the oxygen electrode were also analyzed and a fit was obtained. These values can be found in Table 6.5. The error in fitting values is in the order of 10⁻⁸-10⁻⁹ in terms of χ².

Table 6.5: Comparison of the fit under different gas compositions, R in Ωcm², fs in Hz.

<table>
<thead>
<tr>
<th>Case</th>
<th>R0</th>
<th>R1</th>
<th>fs1</th>
<th>R2</th>
<th>fs2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>fs5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.12</td>
<td>0.053</td>
<td>7570</td>
<td>0.016</td>
<td>2332</td>
<td>0.011</td>
<td>1E-10</td>
<td>0.032</td>
<td>4.09</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>0.057</td>
<td>6464</td>
<td>0.016</td>
<td>4760</td>
<td>0.019</td>
<td>0.008</td>
<td>0.037</td>
<td>3.76</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>0.085</td>
<td>4845</td>
<td>0.016</td>
<td>6968</td>
<td>0.011</td>
<td>1E-10</td>
<td>0.051</td>
<td>4.25</td>
</tr>
</tbody>
</table>

Case 1: 50% H₂O + 50% H₂ on the fuel electrode and O₂ on the oxygen electrode
Case 2: 50% H₂O + 50% H₂ on the fuel electrode and air on the oxygen electrode
Case 3: 20% H₂O + 80% H₂ on the fuel electrode and O₂ on the oxygen electrode

Data fitting for the fuel electrode arc displays inconsistency, however, the magnitude of resistances is similar to the literature values [57]. From the values in the Table 6.4, it is visible that there is a trend in pressure dependency up to 5 bars, after which it is inconsistent. To elaborate, on increasing pressure from 1 to 5 bar, the gas conversion resistance remains similar with a variation of less than 10%. Gas conversion is independent of pressure while the TPB resistance depends on the kinetic energy of gases at the TPB. Furthermore, the total R_p decreases with increase in pressure as expected since the processes are activated easily at higher pressures. For the case of 8 and 10 bars, an increase in gas conversion arc is observed. This can be linked to the decrease in OCV leading to change in gas conversion due to leaks. Furthermore, an increase in both fuel and electrode processes is seen in terms of R1 and R3 which might be caused by change in gas conversion. An increase in R_s is observed throughout. From 1 to 5 bar, a clear dependency on the temperature can be seen from Table 6.1. For 8 and 10 bar, the R_s increase indicates increase in leaks. A fit spectra is shown in Figure 6.8. As can be seen that the modeled values fit well with the raw impedance spectrum. Furthermore, in Figures 6.9 and 6.10, the circuit elements are displayed in the form of Nyquist and Bode plot, along with KK-
transform mapping in Figure 6.11 which substantiates the fit. Given this, the data fitting might be considered to a reasonable extent to draw conclusions on the pressure dependency and leak effects for the cell tested in this work.

The fit for all the elements was easily distinguished. The gas conversion arc was modeled as an R-C circuit, RQ5(CONV), with values of approximately 0.002 Ω cm$^2$. Diffusion, RO4(DIFF), was modeled as RQ circuit with significantly lower resistance than other elements, in the order of $10^{-10}$ Ω cm$^2$. For the oxygen electrode, G3(EL), the value of resistance was in the order of $10^{-4}$ Ω cm$^2$. For the fuel electrode responses, RQ1(EL) and RQ2(EL), the resistances were in the range of 0.0025 to 0.004 Ω cm$^2$. Major contribution is found in the high frequency fuel electrode arc from

**Figure 6.8:** Measured vs. fit data at 10 bar with 50% H$_2$O + 50% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.
modeling due to ionic transport. However, the TPB resistance remains constant which is not as expected and the fitting of the total fuel electrode response is considered.

**Figure 6.9:** Nyquist plot with the fit data at 10 bar with 50% H$_2$O + 50% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

**Figure 6.10:** Bode plot with the fit data at 10 bar with 50% H$_2$O + 50% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

**Figure 6.11:** KK transform of the fit data at 10 bar with 50% H$_2$O + 50% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C.

From the fitting data, it is evident that a correlation between pressure and summit frequencies of the electrode responses exists. Furthermore, the data obtained at 8 and 10 bar are inconsistent due to the presence of leaks which is seen in the form of lowering of OCV. Additionally, the behaviour of the TPB reactions are investigated to understand the relation between pressure and the nature of the reactions taking place. Previously,
research has been done on electrodes under pressure to understand the dissociative adsorption theory [58]. According to this theory, increasing the pressure of the system increases the probability of ions reaching the TPB. However, not all of these can get adsorbed at the TPB. There is a ratio between incoming ions which take part in the reaction and the ones which are not adsorbed. According to Thomsen et.al, this ratio for LSM-YSZ electrodes depends on the partial pressure of oxygen to the power of -0.25. The ratio between the TPB resistances follows a power law with respect to the system pressure. The equation is as follows:

\[ \frac{R'}{R} = \left( \frac{P'}{P} \right)^{-n} \]  

where, \( n \) denotes the order of the reaction at TPB

Since the fitting reveals the TPB resistance to be constant, the combination of TPB and high frequency (ionic rail) resistance is considered for this calculation in this work. The calculation was performed for 3 and 5 bars. The value of \( n \), so obtained, was varied between 0.1 to 0.13. The value of 0.25 denotes complete dissociative adsorption, as explained in literature [58]. This value is related to the LSM-YSZ composite electrode as performed in the work by Thomsen et.al. In this PhD, LSC-CGO electrode was used which might also reflect in the behavior of TPB reaction with pressure. Fundamental studies on LSM-YSZ media have been previously reported [59] and a reaction order of approximately 0.3 was obtained. The value obtained in the work is not complete, owing to the lack of data set and also due to the inaccuracy of fitting. Nevertheless, the behaviour indicates the mechanism which might be responsible for the reactions at TPB.

### 6.4 Conclusions

In this chapter, a high pressure test aimed at obtaining steam electrolysis up to 10 bars was performed. The data reveals correlation between pressure and polarization resistances, especially up to 5 bars. The data obtained at 8 and 10 bar indicate presence of leaks, which is also seen in the form of \( R_s \) increase. A fit indicates the change in response of the fuel electrode TPB reaction with respect to pressure. Furthermore, the fit has been verified by varying gases on individual electrode to underline the consistency. A relationship between the pressure of the system and TPB resistance is obtained with the power law.
CHAPTER 7

System studies: Power-to-Gas, Power-to-Liquid scenario with SOEC

7.1 Introduction

For the sector coupling using SOECs for co-electrolysis, it is of essence to look at the system integration. In this aspect, a detailed electrochemical model for the SOEC also needs to be implemented in order to achieve syngas/methane as an end product. In this context, the production of methane internally in a SOEC under pressurized conditions has previously been demonstrated at DTU, wherein a SOEC stack tested at 18.7 bar has shown significant internal methane production (18% of dry gas out of SOEC at 700 °C) [25]. The need for more investigation of such a system where a SOEC can be connected to the grid to study its potential of conversion and efficiency into methane is evident. Following this, process modeling was performed in this work on the system level to carry out sensitivity analysis on various parameters affecting the system efficiency. A combination of modeling and experiments would serve better, wherein the experiments can be useful in model validation and enhance the analysis. Modeling helps in the prediction of system performance without overlooking the minute details on the cell/stack level.

To briefly discuss the modeling at the cell/stack level to the system level, 0D modeling is used preferably where only the input and output are analyzed [60]. In the case of the cell model, sensitivity analysis can be carried out based on the geometry of the cell/stack [61]. 0D model can not, however, model the variation between the cells in a stack [60]. Furthermore, it lacks versatility owing to the fact that an average value for parameters such as temperature, is assumed on the whole volume [62].

To account for the geometrical aspects, 1D and 2D models are also commonly established and experimentally calibrated. This is done by defining discrete flows along the directions in flow channels and considering a laminar mass transport through the volume such that interactions depend on the spatial flow. This has an effect on the system performance [62, 63].

A more sophisticated model comprises of 3D system modeling, where assumptions need not be simplified. However, it demands considerable computational requirements and cost and is obsolete for the case of dynamic analysis while a certain operating condition can be investigated to the infinitesimally small detail level [61, 64]. In this regard, some valid assumptions can be made to reduce the complexity and
computational requirements yet being able to investigate the electrochemical parameter by means of 1D and 2D models.

During the operation of SOEC, CO\textsubscript{2} and H\textsubscript{2}O are fed to the fuel electrode while O\textsubscript{2}/air is fed to the oxygen electrode. During the splitting of CO\textsubscript{2} and H\textsubscript{2}O electrochemically, the reaction at the triple surface boundaries (TPBs) takes place as well as diffusion of the ions is simultaneously occurring. For modeling the reactive-transport in a multicomponent mixture, Fick’s model (FM) [65–67], Stefan-Maxwell model (SMM) [65, 68, 69] and Dusty Gas model (DGM) [65, 68, 70] have been widely used. FM is quite useful for binary mixtures and is indeed the simplest diffusion model which considers diffusion and convection transport. However, for ternary or multi-component mixtures, the molecular interactions cannot be neglected, which is done in FM, and hence Stefan-Maxwell model (SMM) is used. However, it fails to consider the collision of gas species with the porous media. Hence, DGM encompasses all the possible interactions and collisions with high accuracy. The model assumes that the pore walls consist of giant molecules (‘dust’) which are distributed in space uniformly. Kinetics of the reactions along with diffusion using Dusty Gas model is widely used by authors to model fuel transport through porous fuel cell electrode, taking place during the operation of the cell [71–75]. This allows for the assessment of the thermodynamic as well as microstructural parameters obtained from the cell. Elementary kinetics at the molecular level by considering water gas shift and steam reforming reactions have been investigated previously [71, 76–81]. However, at ambient pressure, hardly any methane is formed and testing under pressurized conditions is required to observe a significant amount of methane. Thermodynamically, methane formation increases with an increase in pressure and a decrease in temperature [53]. However, internal methanation experimental studies in SOEC are limited [25, 82]. In addition, a model for the split of current has been reported based on experimental data validation, wherein surface coverage related to the molar fraction of species determines the proportion of current between two reactions. This has also been used by various authors in their electrochemical model of co-electrolysis using SOEC [71, 83, 84].

In this work, a SOEC operating under co-electrolysis is modeled. The system modeling was performed as a part of the project at EPFL, Switzerland [85]. The electrochemical modeling of SOEC along with model calibration with the validation of experimental data was performed as a part of this PhD, along with DGM to account for diffusion in porous media are implemented to account for the interaction at molecular level. A quasi 2D model is implemented to consider the molecular phenomenon for the SOEC using ASPEN+ custom modeler. It does not account for the effect of catalyst loading and aging of the cell/stack. Both electrodes and electrolyte are segmented in X- and Y-directions, as illustrated in Figure 7.1, while the gas channels are only segmented at the X-direction. Note that with such segmentation, mass transportation is considered to occur only at Y-direction: locally-produced and are not dispersed to neighboring segments at X-direction but only dispersed vertically back to the corresponding gas-channel segment. The effect of operating pressure on the electrolyser performance is considered. To account for the activation parameters,
the experimental data is validated with the model. Based on the results, splitting of the current density along the channel direction is investigated.

Figure 7.1: Layout of the SOEC model [85].

7.2 Methodology

For the modeling of the SOEC cell/stack, for the cell dimensions, data are collected from different experimental setups involved in the EU-ECo project namely DTU, EIFER and SOLIDPower. Based on the experimental data, a model is designed considering parameters such as the thickness of electrolyte, individual electrodes, length of the feed flow channel and width of the electrode. Typical configuration of a fuel electrode based solid oxide cell are considered with fuel electrode properties, namely, porosity, tortuosity, average particle diameter, pore radius and specific area. In this section, equations related to the model based on material parameters for SOEC are presented based on values from literature. Based on the material parameters, the permeability coefficient (B) for the cell for ionic transport is calculated as:

\[
B = \frac{\epsilon^3 \ast dp^2}{72 \ast \tau \ast (1 - \epsilon)^2}
\]  

(7.1)
where, $\epsilon$ is the porosity of the material, $dp$ is the pore diameter, and $\tau$ is the tortuosity. Since the kinetics of binary mixtures are considered, average molecular weight is calculated of a binary mixture:

\[
M_{ij} = \frac{2}{\frac{1}{M_i} + \frac{1}{M_j}} \quad (7.2)
\]

where, $i$ and $j$ represent the species and $M$ is the molecular mass.

Similarly, for a binary mixture of species, average characteristic length is calculated as:

\[
\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (7.3)
\]

Average Lennard-Jones characteristic length is given as:

\[
\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (7.4)
\]

Average tortuosity is calculated as:

\[
\tau = \frac{kT}{\epsilon_{ij}} \quad (7.5)
\]

Collision integral is calculated by the following equation:

\[
\Omega_D = A + \frac{C}{\exp \left( D\tau \right)} + \frac{E}{\exp \left( F\tau \right)} + \frac{G}{H\tau} \quad (7.6)
\]

where, the values of the constants are provided in the following table

**Table 7.1**: Collision integral constants.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.06036</td>
<td>0.15610</td>
<td>0.19300</td>
<td>0.47635</td>
<td>1.03587</td>
<td>1.52996</td>
<td>1.76474</td>
<td>3.89411</td>
</tr>
</tbody>
</table>

Furthermore, the binary diffusion coefficient is defined using the variables calculated above as:

\[
D_{ij} = \frac{0.0026T^{1/2}}{pM_{ij}^{1/2}\sigma_{ij}^{2/3}\Omega_D} \quad (7.7)
\]

The calculated parameters above relate to the diffusion of the gases through the electrodes of the SOEC. Calculated parameters determine the material properties from the equations stated above. Additionally, a distributed model based on the discretization of the SOEC as displayed in Figure 7.1 is performed to obtain a quasi 2-D model. The channel is divided into N nodes in x-direction and each node is further divided in y-direction. It is assumed that the flow of the fuel is only in y-direction along the
channel/node.

To investigate the electrochemical reactions undergoing in the fuel electrode, kinetics of water-gas shift reaction and steam-methane reforming reaction are applied, while in the fuel channel the assumption of attainment of chemical equilibrium is considered.

Regarding the kinetics of Water gas shift (WGS) and Steam methane reforming (SMR) reactions, temperatures $T_C$ are converted to Kelvin scale $T_K$ and the temperature factor $T_R$ is also calculated as follows:

$$ T_R = \frac{1000}{T_K} - 1 $$

(7.8)

For calculation of rate of WGS reaction, following equations are applied

$$ R_{shift} = k_{shift}(P_{H_2O}P_{CO} - \frac{P_{H_2}P_{CO}}{K_{eq,shift}}) $$

(7.9)

$$ k_{shift} = 0.0171 * exp\left(-\frac{103191}{R_0T}\right) $$

(7.10)

and

$$ k_{eq,shift} = exp(-0.2935T_R^3 + 0.6351T_R^2 + 4.1788T_R + 0.3619) $$

(7.11)

wherein, $p$ represents the partial pressure of the respective species.

For SMR kinetics, three different models are considered:

1. Lehnert [79]
2. Achenbach [86]
3. Leinfelder [87]

According to the Achenbach model, reforming rate is given as:

$$ R_{reform} = 4274(1 - \frac{P_{CO}P_{H_2^3}}{P_{CH_4}P_{H_2O}K_{eq, reformation}})(P_{CH_4})exp\left(-\frac{82000}{R_0T}\right) $$

(7.12)

where,

$$ K_{eq, reformation} = 1.0267*10^{10}exp(-0.2513T_R^4 + 0.3665T_R^3 + 0.5810T_R^2 - 27.134T_R + 3.2770) $$

(7.13)

For Lehnert’s model,

$$ k_{reform} = k_f * k_b $$

(7.14)

where, $k_f$ is the rate of forward reaction and $k_b$ is for the backward reaction. Along with $K_{eq, reformation}$ calculated earlier,$k_f$ is calculated as:

$$ k_f = 2395exp\left(\frac{231266}{R_0T}\right) $$

(7.15)
In theory, the equilibrium constants are the same, regardless of the equations used resulting in same equilibrium concentration of respective species.

For the mass-transport modeling, molecular weight, Lennard-Jones potential, binary diffusion coefficient and viscosity in vapor phase is considered. Considering the water-gas shift reaction kinetics, reaction stoichiometry, reaction rate, saturation pressure at TPB, exchange current density, cell and species current density are pre-defined. For the mass transport, Dusty Gas Model is implemented. The species molar flux ($J_k$) is calculated as:

$$J_k = \left[ \sum_{l=1}^{K_g} D_{kl}^{DGM} \nabla [X_l] + \left( \sum_{l=1}^{K_g} \frac{D_{kl}^{DGM}}{D_{l,Kn}^e} \frac{B_g}{\mu} \nabla [p] \right) \right] (7.16)$$

The first term of the right hand side of the equation represents the diffusive element of the flux while the second term represents the viscous element of the model. Herein, permeability $B_g$ is given according to the Kozeny-Carmen equation as:

$$B_g = \frac{\epsilon^3 d_p^2}{72\tau(1 - \epsilon)^2} \quad (7.17)$$

and DGM diffusion coefficients are given as:

$$D_{kl}^{DGM} = H^{-1} \quad (7.18)$$

where, the elements of H matrix are given as:

$$h_{kl} = \left[ \frac{1}{D_{kn}^e} + \sum_{j \neq k} \frac{X_j}{D_{kj}^e} \right] \delta_{kl} + (\delta_{kl} - 1) \frac{X_k}{D_{kl}^e} \quad (7.19)$$

and the effective Knudsen diffusion coefficient $D_{k,Kn}^e$ is given by:

$$D_{k,Kn}^e = \frac{\epsilon}{\tau} \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi W_k}} \quad (7.20)$$

where, W is the molecular weight of the species.

Furthermore, at the electrode-electrolyte interface calculation of species current density ($J$) is performed locally such that:

$$J_{H_2O} = -J_{H_2} = \frac{I_{H_2}}{2F}, J_{CO_2} = -J_{CO} = \frac{I_{CO}}{2F}, J_{O_2} = -\frac{I_{H_2} + I_{CO}}{4F} \quad (7.21)$$

Herewith, the current densities in terms of flux are set equal. Boundary conditions for flux of individual species is set to the sign of stoichiometry of the reaction taking place according to the mode of operation. Moreover, at the inlet of the channel, pressure and mole fraction are defined. Additionally, molar flux is also calculated according to the respective current densities.

Exchange current density ($J_0^i$) is calculated as:

$$J_0^i = k_i \exp(\frac{-E_a}{RT}) \quad (7.22)$$
Furthermore, the partial pressure of the reacting components also contributes to the exchange current density, depending on the stoichiometry of the reaction taking place. The species’ partial pressure is calculated as:

\[ p_i = \frac{\Gamma}{\gamma_i} \sqrt{2\pi RTW_i k_d,i \exp\left(-\frac{F E_{\text{des},i}}{RT}\right)} \]  

where, \( \Gamma \) is the surface site density
\( \gamma \) is the sticking coefficient

The exchange current density for the individual species are calculated as follows:

\[ i_{0,H_2} = i_{H_2}^* \frac{(p_{H_2}/p_{H_2}^*)^{\frac{1}{2}}}{1 + (p_{H_2}/p_{H_2}^*)^{\frac{1}{2}}} \]  

\[ i_{0,CO} = i_{CO}^* \frac{(p_{CO_2}/p_{CO_2}^*)^{\frac{1}{2}}}{1 + (p_{CO}/p_{CO}^* + (p_{CO_2}/p_{CO_2}^*)} \]  

\[ i_{0,O_2} = i_{O_2}^* \frac{(p_{O_2}/p_{O_2}^*)^{\frac{1}{2}}}{1 + (p_{CO}/p_{CO}^*)} \]  

Additionally, the polarization losses are calculated in terms of Nernst voltage losses using Gibbs free energy of the electrochemical reaction taking place. In the context of the electrochemical parameters, asymmetry factor for individual electrodes along with activation energy and pre-exponential factor related to the Arrhenius equation are considered. For the electrodes, various surface parameters are considered for the calculation of exchange current density. This in turn helps calculate the saturation pressure at the triple phase boundary and the activation data for specific electrochemical reactions taking place.

Activation losses are related to the current density using Butler-Volmer equation \[72\]. For the H\(_2\) electrode:

\[ i_{H_2} = i_{H_2}^0 \left[ \exp\left(\frac{(1 + \beta a) F \eta_c}{RT}\right) - \exp\left(-\frac{\beta c F \eta_c}{RT}\right) \right] \]  

For reduction of CO\(_2\):

\[ i_{CO} = i_{CO}^0 \left[ \exp\left(\frac{\beta a F \eta_c}{RT}\right) - \exp\left(-\frac{(1 + \beta c) F \eta_c}{RT}\right) \right] \]  

For O\(_2\) electrode:

\[ i_{O_2} = i_{O_2}^0 \left[ \exp\left(\frac{\beta a F \eta_c}{RT}\right) - \exp\left(-\frac{\beta c F \eta_a}{RT}\right) \right] \]  

Here, \( \beta \) represents the asymmetry factor for the electrode while \( \eta \) represents the activation energy.

Additionally, ohmic losses are also calculated depending on the resistivity and thickness of the electrolyte and using Ohm’s law:

\[ \eta_{\text{Ohmic}} = i R_{\text{tot}} \]
Concentration polarization is calculated by relating the molar fractions in the bulk and TPBs as:

\[ \eta_{\text{conc}} = \frac{RT}{2F} \ln\left( \frac{y_i, H_2 yH_2O}{y_i, H_2O yH_2} \right) \]  

(7.31)

where \( y \) is the mass fraction of the species.

Overall voltage is calculated as:

\[ V = E - \eta_{\text{conc}} - \eta_{\text{act, fuel electrode}} - \eta_{\text{act, oxygen electrode}} - \eta_{\text{Ohmic}} \]  

(7.32)

wherein, all the losses taking place through the polarization curve are considered in the model. This includes material properties, overpotentials, kinetics and mass transport.

### 7.3 Results and Discussion

#### 7.3.1 Model calibration results

For the calibration of the model, data pertaining to both steam and co-electrolysis are utilized. Based on these data sets, values for the inlet temperatures for fuel and air/oxygen, molar fraction of components, voltage and current density were acquired. Apart from the current density, the other variables are set as fixed parameters while the current density for the i-V curve was estimated since parameter estimation relies on the versatility of experimental data points.

In this section, the model calibration results are represented. The estimated i-V curves are plotted alongside the measured i-V curves to represent the precision of estimation. The cell was firstly calibrated for steam electrolysis and is further also analyzed with the fuel cell data to assure the robustness of the current model.

For the case of steam and co-electrolysis with oxygen flow on oxygen electrode at 1 bar, data is taken from the SoA cell tested at DTU. A comparison of the predicted and the measured variables, current density in this case, is shown. For the case of steam electrolysis, a good estimation was obtained without including the kinetics in the model, since no WGS or SMR reaction occurs for the steam electrolysis. However, for the case of co-electrolysis, the prediction improves by including kinetics in the model, especially at current densities above 1 A/cm\(^2\). By including the WGS reaction kinetics, the fuel starvation issue is resolved, due to the local production of potential electrochemical reactants.

In addition, i-V curves are estimated under different conditions to assess the quality of agreement between the predicted and experimental data sets. In Figure 7.2, i-V curves are estimated both with and without kinetics under two different gas compositions and at three different temperatures. i-V curves are estimated for co-electrolysis conditions without and with kinetics incorporated in the model.
Figure 7.2: i-V curves for the SoA cell with 90% H₂O + 10% H₂ on fuel electrode (a) without, and (b) with kinetics; with 50% H₂O + 50% H₂ on the fuel electrode (c) without, and (d) with kinetics.

In Figure 7.3 (a) and (b), similar estimation is observed at all temperatures depicting the model can predict the experimental results to a good extent even without including kinetics. However, a significant improvement at high current densities is observed for Figure 7.3 (c) and (d), after including water gas shift kinetics. This is observed for all the temperatures as the kinetics can estimate the local fuel concentration limitation and hence the overall model with kinetics included can estimate both steam and co-electrolysis for a full cell.
7.3 Results and Discussion

Figure 7.3: i-V curves for the SoA cell with 65% H$_2$O + 25% CO$_2$ + 10%H$_2$ on fuel electrode (a) without, and (b) with kinetics; with 45% H$_2$O + 45% CO$_2$ + 10% H$_2$ on fuel electrode (c) without, and (d) with kinetics.

Once the parameter estimation for the cell is performed, the model was tested for scaling by using the data for SoA stack. The tests were performed at EPFL with varying the fuel composition with air on the oxygen electrode. A comparison of the estimated values for SoA stack under steam and co-electrolysis, respectively, are shown. It is interesting to note that the predicted values are already coherent with the experimental values without including kinetic parameters. On inclusion of the kinetic parameters, however, at high current densities a deviation is observed. In Figure 7.4 and Figure 7.5, the i-V curves show good coherence without kinetics while inclusion of kinetics shows a deviation in the prediction at high current density for co-electrolysis case, especially in Figure 7.5(d).

This implies that the model can predict the behavior of the cell quite comprehensively, while the local concentration gradient of the stack shows a different behavior owing to the fuel distribution along the channel. This concentration loss can be further improvised; however, the estimation shows that the model is suitable for a cell and a stack performance prediction under nominal conditions.
Figure 7.4: i-V curves for SoA stack with 90% H₂O + 10% H₂ on the fuel electrode (a) without, and (b) with kinetics.

Figure 7.5: i-V curves for SoA stack with 65% H₂O + 25% CO₂ + 10% H₂ on the fuel electrode (a) without, and (b) with kinetics; with 50% H₂O + 39% CO₂ + 11% H₂ on fuel electrode (c) without, and (d) with kinetics.
7.3.2 Sensitivity Analysis

Thermodynamically, the production of methane at atmospheric pressure under high temperature conditions is rather difficult using a SOEC. Ideally, CH$_4$ can be produced at temperatures under 350 °C using Fischer-Tropsch process [53]. Literature studies have reported that for a fuel electrode supported SOEC, the methane fraction is less than 0.5% (based on dry gas out of the SOEC) with the operating temperature ranging between 550–650 °C [88]. Furthermore, addition of Ru based catalyst as a promoter for methane production, leads to an observed methane fraction of 0.077% at 650 °C experimentally [88]. The equilibrium constant of the SMR reaction is plotted in terms of temperature in Figure 7.6.

![Equilibrium constant of the SMR reaction](image)

**Figure 7.6:** Equilibrium constant of the SMR reaction.

The experimental tests performed in EU-Eco at CEA also revealed that the methane production in SOEC was below 0.1% (dry gas composition) at atmospheric pressure and 800 °C. An increase in pressure to 3.7 bar and a decrease in temperature to 750 °C significantly promotes the methane production to 0.2%.

The experiments have been performed at relatively low pressures (below 5 bar), which do not reveal the pressure effect on the direction taken by the reaction. The kinetics of the SMR reaction applied to the modeling does not take into account the effect of pressure. As a result, an equilibrium calculation for each segment in the gas channel of X direction was performed as shown in Figure 7.1. For the fuel electrode, the kinetics were taken from literature due to inadequate data and limited methane production observed at CEA, which may hardly support the calibration of steam-methane reforming reaction and may lead to biased parameter estimation.

A sensitivity analysis by varying the following variables:

- inlet temperature between 550 – 800 °C,
- operating pressure between 1 – 30 bar,
7.3 Results and Discussion

- steam feed flowrate between 4 – 12 Normal millilitre per minute (NmLPM)/cm²,
- overall utilization factor (10 – 80%),
- anode/cathode feed ratio (0 – 4)

The model is designed for an adiabatic SOEC operation considering the variables mentioned above in order to calculate the operating voltage and the current density as well as the outlet temperature for suitable methanation gas flow. For a high methane production in a SOEC, the operation at a higher current density is not adapted since it leads to high voltage, therefore increasing the stack temperature due to heat release. Furthermore, the increase in temperature leads to a decrease in methane production.

7.3.2.1 Effect of operating temperature

Temperature is varied keeping the utilization factor at 20%, operating pressure of 1 bar, steam feed flowrate of 12 NmLPM/cm², and anode/cathode feed ratio of 1. The results are plotted in Figure 7.7. Internal methane production at temperatures as low as 700 °C is only 0.05%. On decreasing the inlet temperature, an increase in internal methane production is expected and the highest methane fraction is observed between 600–620 °C. The molar fraction, however, is lesser than the experimental results due to the adiabatic conditions and higher outlet temperature (670 °C) than inlet temperature during simulation. Reduction in the temperature has no significant effect on direct internal methane production.

Figure 7.7: Temperature effect on the internal methane production (pressure 1 bar, current density 0.39 A/cm², steam feed flowrate 12 NmLPM/cm², fuel electrode/oxygen electrode ratio 1).
7.3.2.2 Effect of operating pressure

For the temperatures of 620 °C and 700 °C at inlet, with 20% utilization factor, steam feed flowrate of 12 NmLPM/cm², anode/cathode feed flowrate of 1, the sensitivity analysis on the effect of pressure from 1 to 30 bar is performed. The results are displayed in Figure 7.8. Operating at 30 bar, up to 8% methane can be formed in dry gas thermodynamically. The decrease in methane production by increasing the temperature from 620 to 700 °C is not significant. When the inlet compositions are defined for experiments manually, such an effect is not visible. It has been observed that the H₂ content of syngas produced from SOEC in experiments is low, which lowers down the pressure effect on internal methanation. During simulation, however, the inlet composition is adjusted to be suitable for methanation with H₂ content being approximately 70%. High H₂ content leads to a significant effect of pressure on methanation. Increasing pressure is required for promoting internal methanation and its effect is more pronounced than reducing the temperature.

![Figure 7.8: Pressure effect on internal methane production (inlet temperature 620 °C, 20% utilization factor, steam feed flowrate of 12 NmLPM/cm², fuel electrode/oxygen electrode feed flowrate of 1) (a)Inlet temperature 620 °C (b)Inlet temperature 700 °C.](image)

7.3.2.3 Effect of inlet feed flows (current density)

If the fuel utilization is fixed, the effects of SOEC feed flows and operating current density are in fact similar. For the sensitivity of inlet feed flows, the steam feed is varied between 4 – 15 NmLPM/cm² with the fixed inlet temperature 700 °C, pressure...
30 bar, utilization factor 20% and the fuel electrode/air electrode feed flowrate of 1. For achieving the utilization, increasing steam feed needs a higher current density as shown in Figure 7.9(a), leading to higher operating voltage and thereby higher overpotentials as displayed in figure 7.9(b). As a consequence, the outlet temperature also increases. This leads to a decrease in methane production since an increase in H$_2$O content in the outlet gas mixture is observed, hindering the internal methanation reaction. It is worth noting that with a small steam feed of 4 NmLPM/cm$^2$, 20% reactant utilization, 30 bar operating pressure and 700 °C inlet temperature, the direct methane yield can contribute 12% to the SOEC outlet gas with an outlet temperature of 630 °C.

Figure 7.9: Effect of the operating current density on internal methane production (inlet temperature 700 °C, pressure 30 bar, 20% utilization factor, anode/cathode feed flowrate of 1) (a)steam feed vs. current density and outlet temperature (b)Steam feed effect on direct methanation.

7.3.2.4 Effect of the reactant utilization

To investigate the effect of the reactant utilization, the range of 20-80% is used along with inlet temperature 700 °C, pressure 30 bar, steam feed flow 4 NmLPM/cm$^2$, and fuel electrode/oxygen electrode feed ratio 1 is employed in Figure 7.10. To increase the utilization, the current density needs to be increased leading to higher stack voltage, higher overpotential and higher stack outlet temperature as shown in Figure 7.10(a). Higher utilization leads to higher conversion of steam into H$_2$, leading to higher methane production and positive effect of pressure. With a reactant utilization of 80% for a steam feed 4 NmLPM/cm$^2$, 23% methane fraction in the dry outlet gas of
a SOEC can be achieved.

Figure 7.10: Effect of the reactant utilization on internal methane production (inlet temperature 700 °C, pressure 30 bar, steam feed flow 4 NmLPM/cm², fuel electrode/oxygen electrode feed flowrate of 1) (a) Reactant utilization vs. current density/outlet temperature (b) Reactant utilization effect.

7.3.2.5 Effect of anode/cathode ratio

The effect of the oxygen electrode to the fuel electrode feed i.e., anode/cathode feed ratio was performed in the range of 0 to 4, with an inlet temperature 700 °C, pressure 30 bar, steam feed flow 4 NmLPM/cm² and a utilization factor 80%. Increasing sweep air flowrate reduces the stack temperature as shown in figure 7.11(a), thereby increasing internal methane production as seen in Figure 7.11(b). If enough cooling is provided, methane content of 25% can be achieved in dry outlet gas of the SOEC.

Figure 7.11: Effect of the reactant utilization on internal methane production (inlet temperature 700 °C, pressure 30 bar, steam feed flow 4 NmLPM/cm², utilization factor 80%) (a) Reactant utilization vs. current density/outlet temperature (b) Reactant utilization effect.
7.4 Conclusions

A comprehensive discretized model is designed for SOEC to be operated in both steam and co-electrolysis conditions. Both the thermodynamic and the electrochemical parameters are considered for the design. For model calibration, data sets for both steam and co-electrolysis are utilized as obtained under various operating conditions of pressure, temperature, and fuel and oxygen electrode composition. Both the cell and the stack models can be predicted to a good degree of certainty thereby implying that the model can be scaled from cell to stack level. This is further seen through i-V curves for each case, thereby ascertaining the precision of the model calibration. The optimal operating conditions to maximize the internal methanation production is indicated by low temperature and high pressure operation. Particularly, the reaction is boosted when the gas mixture is with high H₂ content and low steam content. The optimal operating conditions can be then defined as:

- inlet temperature of 700 °C,
- operating pressure of 30 bar,
- steam feed flowrate of 4 NmLPM/cm², CO₂ feed rate of 1.22 NmLPM/cm²,
- overall utilization factor of 80%,
- anode/cathode feed ratio of 4

The obtained outlet gas composition on a dry basis in terms of mole fraction is CH₄ 0.2895, CO 0.1160, CO₂ 0.0478, H₂ 0.5442, H₂O 0.0025.
In this thesis, SOECs were tested and characterized for the purpose of co-electrolysis to produce methane. The concept of sector coupling in order to use SOECs with varying wind profile to match the demand and supply was investigated. The integration of energy storage via SOECs and wind profile has been demonstrated both on the cell and the stack level, in this PhD. To begin with, the SOECs were analyzed experimentally while modeling on system level was performed for optimization of methane production. This thesis contains excerpts from testing modes, electrode modifications, dynamic energy storage and pressurized testing which are summarized in this chapter. The aim of this work was to understand the degradation and enhance the performance and lifetime of SOECs. Furthermore, the limitations in the setup are also discussed. Ultimately, an electrochemical model for SOEC is developed using the test data is used for validation of cell parameters.

8.1 Comparison of testing modes-galvanostatic vs. potentiostatic

To analyze the effect of the testing modes, SoA cells were firstly characterized under galvanostatic and potentiostatic modes for a comparison of the degradation mechanisms. Initial degradation was similar for both modes. The most interesting aspect of this study arose from the comparison of ASR in two different modes. The increase in both ohmic and polarization resistance was seen for galvanostatic mode leading to increased overpotential on the electrodes. For the potentiostatic testing, the overpotential remained same leading to increase in only polarization resistance. As a result, the potentiostatic mode serves to protect the cell by lowering the current density which may lead to longer lifetimes.

8.2 Degradation analysis-electrode modification and the effect of current densities

In order to improve the performance of SOECs, the concept of modification of electrodes was studied for both the electrodes. The cells were tested potentiostatically. For the oxygen electrode, the infiltration of LSC on CGO backbone was taken up. The cell obtained herewith, displayed lower performance and increased ASR which was related to non optimized infiltration through post-test SEM. For the fuel electrode, particle size distribution was changed leading to an increased performance of
the cell. The degradation trend also was rather linear as opposed to the other cells tested prior in this work where higher degradation was observed in the first 200 hours.

### 8.3 Dynamic cycling and effect of current density

After obtaining an improved cell through electrode modification, the idea of implementing dynamic energy storage was used for testing a cell and a stack. The cell was tested first, which displayed degradation of the fuel electrode. Furthermore, current densities up to 0.75 A/cm$^2$ were applied leading to severe degradation of the cell. It was then desired to operate the stack with lower current densities i.e., maximum current density of 0.5 A/cm$^2$ was applied. Herein, marginal degradation of the fuel electrode was observed. Interestingly, the average cell voltage degradation decreased from 15%/1000 h at the cell level to 0.8%/1000 h at the stack level. The stack also served as a constant source of H$_2$ and syngas.

### 8.4 High pressure testing and its effect on leaks

Due to the limitations in the test setup, only steam electrolysis was performed under pressurized conditions for the improved cell. The cell was pressurized up to 10 bars and evolution of ASR and polarization resistance in particular was analyzed. The cell showed decrease in ASR up to 5 bars after which leaks led to a change in gas conversion leading to an increase in ASR. Furthermore, data fitting led to the correlation between electrode performance and pressure. Interestingly, leaks were observed in all the tests in this PhD work, since the H$_2$ content was only kept at 10%, where even a small change in gas conversion was clearly visible. An analysis of the cells tested in this work as well as from the data collected earlier at DTU indicated the nature of leaks to be a combination of both hydrogen and oxygen gas diffusion along with a flow dependency. The pressurized set of data led to the development of an empirical model for leaks under such systems.

### 8.5 Electrochemical modeling of SOEC with experimental data

A model for steam and co-electrolysis was developed as a tool for parameter prediction for optimized case of methane formation. The electrochemical cell model was calibrated with the experimental data obtained on cell and stack level. Furthermore, sensitivity analysis indicated a need for pressurized operation under lower temperatures for a high internal methanation output. A temperature of 700 °C at 30 bar pressure with a utilization factor of 80% was indicated as optimal leading to approximately 29% of methane yield on dry basis.

This thesis serves as a reference for energy storage in PtL/PtG scenario with regards to optimum operating conditions from both modeling and experimental data along with a comprehensive understanding of degradation mechanisms for SOECs.
This PhD project aims at methane production using SOECs wherein the concept of dynamic energy storage is analyzed. One of the important aspects relates to the electrode structure of the cell. In this work, the oxygen electrode modification did not deliver desirable results. Optimization of infiltration technique as well as infiltrate backbone adhesion needs to be investigated in detail in the future.

A major outcome of this work led to the understanding of potentiostatic mode of operation in order to protect the cell from severe degradation. Thermodynamically, it is desired to operate SOECs at thermoneutral voltage. For a 65% H$_2$O + 25% CO$_2$ + 10% H$_2$ fuel gas composition, a thermoneutral voltage of 1.33 V is obtained. Since the cells in this work were tested at 1.2 V, further testing and characterization at thermoneutral voltage along with effect of current density and overpotential on the electrodes need to be studied.

Modeling results predicted internal methane formation at 30 bar which need to be experimentally determined. High pressure testing under co-electrolysis conditions with a gas chromatograph to analyze the outlet gas composition would lead to the validation of simulated work. This can further be used to improvise the model to fit the experimental testing conditions. Additionally, the dynamic testing under pressurized conditions could give an insight into methane production in a real-case scenario.

This PhD also discusses the effect of leaks briefly. Data mining led to the revelation that cell tests conducted for 4*4 cm$^2$ cell under high steam and co-electrolysis conditions displayed leaks. More analysis into the nature of leak and its effect on performance and electrode overpotential need to be investigated. Additionally, pressurized test results can be used to investigate the relationship between pressure and the nature of TPB reactions fundamentally on LSC-CGO electrodes.


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A Comparative Study of Durability of Solid Oxide Electrolysis Cells Tested for Co-Electrolysis under Galvanostatic and Potentiostatic Conditions
A Comparative Study of Durability of Solid Oxide Electrolysis Cells Tested for Co-Electrolysis under Galvanostatic and Potentiostatic Conditions

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State-of-the-art SOECs consisting of a nickel-yttria stabilized zirconia (Ni-YSZ) fuel electrode, YSZ electrolyte and lanthanum strontium cobaltite ferrite-gadolinium doped ceria (LSCF-GDC) composite oxygen electrode were tested under co-electrolysis (H2O-O2-CO2) conditions. The aim in this study was to compare the SOEC durability under galvanostatic and potentiostatic conditions. Specifically, the cells were operated at 0.75 A/cm2 (galvanostatic) and at 1.2 V (potentiostatic) at 800°C for 200 hours of testing. In both modes, a larger degradation was observed initially for the first 200 hours of testing, followed by a more stable performance over longer operating times. Interestingly, there was a difference in trends of serial and polarization resistances’ evolution. In galvanostatic mode of operation, both increased while for potentiostatic mode only the polarization resistance increased over time. The difference of the degradation attributed to the overpotentials being experienced by the cells in the respective modes. Trends of the area-specific resistance (ASR) and detailed electrochemical analysis of the performance of the cell under durability conditions for both modes indicated that the degradation was due to both the fuel electrode and the oxygen electrode, with an additional contribution from fuel electrode in galvanostatic testing. Microstructural analysis also confirmed the degradation of the active fuel electrode.

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Manuscript submitted April 12, 2018; revised manuscript received June 11, 2018; Published June 30, 2018. This was Paper 1717 presented at the National Harbor, Maryland Meeting of the Society, October 1-5, 2017.

For the past few decades, the use of renewable energy sources for power production has been increasing. Europe aims at producing most of its electricity through renewable energy sources by 2050, lowering greenhouse gas emissions significantly as a consequence.1 Solar and wind energy have already acquired the status of matured technologies for renewable electricity production.2,3 The larger shares of electricity from these fluctuating sources require efficient electricity storage technologies. Some of the examples of such available storage technologies are compressed air, batteries and flywheels.4 In this context, fuel cells and electrolysis cells become interesting for both, energy production and storage. Especially, high temperature electrolysis using solid oxide electrolysis cells (SOECs) has gained significant interest, owing to the capability to convert CO2 and H2O to produce syngas (CO + H2).5-6 Power-to-Gas (PtG) and Power-to-liquid (PtL) scenarios have gained significant attention in the past few decades. In case of renewable energy production, intermittent energy can be stored in the form of gas or liquids through fuel production from syngas.7-9 The motivation of using SOECs in the context of PtL and PtG solutions is due to its high electrical efficiency, up to 100%. To perform electrolysis operation, the required energy is provided partly by the high temperature operation of SOEC and the remainder is provided by electricity.10 While operating SOECs in co-electrolysis mode, syngas is produced which can be further converted downstream into various fuels which can be used for energy storage, transportation, heating etc.5,6,7 In the context of PtG technology, production of methanol is of particular interest due to the existing extensive infrastructure for storage and distribution.11-12 An interesting aspect of co-electrolysis operation using SOEC is internal methane formation at high pressure.10 However, limited studies have been carried out in this field.13

Aiming at 5–10 years of operation, durability of SOECs is still one of the major challenges. SOEC cells have previously been reported for both steam and co-electrolysis conditions.2,14-15 The cells have been tested for thousands of hours under different testing conditions such as temperature, gas composition and applied current.16-19 From a system point of view, it is desirable to operate SOEC at thermoelectric voltage, i.e. the voltage where no additional heat is required for the electrolysis reaction. However, due to the technical ease of galvanostatic operation and data analysis, most tests have been carried out in this mode.20 Studies of degradation mechanisms under potentiostatic operating conditions are rare.21 Comparison of the durability and degradation mechanisms between galvanostatic and potentiostatic operation has not been widely reported in literature.

In this work, SOEC cells consisting of Ni-YSZ fuel electrode support, Ni-YSZ fuel electrode, YSZ electrolyte, GCG barrier layer and LSCF-GDC oxygen electrode were tested for ca. 1000 hours for durability under co-electrolysis conditions in galvanostatic and potentiostatic modes. Post-test SEM analysis was carried out to analyze the microstructural changes after long-term testing. Both electrochemical and microstructural analyses were used to identify the detailed degradation mechanisms in both modes.

Experimental

Three SOECs from HTceramix consisting of a Nickel-Yttria Stabilized Zirconia (Ni-YSZ) fuel electrode with a thickness of 220–260 μm, a 6–10 μm thick YSZ electrolyte, a GCG inter-diffusion barrier layer and a 40–60 μm thick composite oxygen electrode of lanthanum strontium cobaltite ferrite-gadolinium doped ceria (LSCF- GCG) were tested. The active area of the cells was 16 cm2.

The cells were tested in a setup as described in Refs. 21, 22. They were mounted in an alumina cell test house with gold and nickel as current collector contact components on the oxygen and fuel side, respectively. A gold sealing was used on the fuel side. 4 kilograms of weight was applied on top of the cell house during start-up to ensure gas tight seals and electrical contact between the cell and the contact components. The cells were heated to 800°C, at a ramp rate of 60°C/A, and held for 2 hours prior to reduction. During heating, N2 and air were supplied to the fuel electrode and oxygen electrode compartment, respectively. The cells were reduced with N2 and H2 beginning from 90% N2 for 1 hour, eventually shifting the flow to pure H2 for 1 hour on the fuel electrode. On the oxygen electrode, a constant air flow was maintained. Initial electrochemical characterization of the cell was performed afterwards.

Three cells were tested, named Cell A, Cell B and Cell C. Cell A only experienced reduction and an initial electrochemical characterization (fingerprint), while Cell B was tested galvanostatically and Cell C was tested potentiostatically for ca. 1000 hours. The fingerprint is an electrochemical characterization of the cells at 800°C, 750°C,

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700°C and 650°C. At each temperature, i-V characterization and EIS measurements were performed with either air or O₂ supplied to the oxygen electrode. The steam content was varied as 4%, 20%, 50%, 80% and 90% with H₂ on the fuel electrode. Furthermore, the air or coal gas mixture was carried out with 40% H₂O+30% CO₂+10% H₂, 45% H₂O+45% CO₂+10% H₂, and 65% H₂O+25% CO₂+10% H₂ supplied to the fuel electrode compartment. EIS measurements during finger printing were carried out at zero DC current using a Solarton 1255 frequency analyzer and an external shunt resistor in series with the cell. The spectra were recorded from 90850 to 0.08 Hz with 12 points per decade and were corrected using the short circuit impedance response of the test setup. A short-circuit impedance response for compensation of EIS was measured without the cell test house. i.e. by short circuiting the current and voltage wires outside of the furnace. Therefore the impedance here was mainly due to the current leads on cell test house and the current leads, which is not identical in all the tests. From the impedance spectra, the ohmic resistance (series resistance, Rs) was taken as the value of the real part of the impedance at 9860 Hz. Typically the Rs is obtained from the intercept of the Z’-axis, however, as previously reported by Sun et al., the calculation of Rs as done in this work provides a more correct value. The difference between the intercept and this value is very small. The polarization resistance (Rp) was then calculated as the difference in the real part of the impedance at 9860 Hz and 0.08 Hz. EIS measurements during durability tests were carried out at 0.75A/cm² for galvanostatic operation and at 1.2 V during potentiostatic operation with a frequency range of 9860 kHz to 0.08 Hz. EIS curves were recorded both in fuel cell (FC) and electrolysis (EC) mode as well as function of the gas composition. For FC mode, the minimum voltage limit was set to 0.60 V while for EC mode the curve maximum voltage was set to 1350 mV. The i-V curves were recorded in 3 parts with step size of 0.25 A, followed by 0.5 A in the linear region and finally 0.25 A. The step size of 0.25 A was maintained until either the current or voltage threshold was reached.

The electrochemical durability testing of the cells was carried out in co-electrolysis mode with 65% H₂O+25% CO₂+10% H₂ in the fuel feed corresponding to 23% CO₂ + 2% CO + 8% H₂ +76% H₂O and equilibrium composition. Cell B was tested galvanostatically at 0.75 A/cm² and 750°C. The fuel utilization was fixed at 48.7% for galvanostatic operation. Cell C was operated under the similar and constant gas composition, potentiostatically at 1.2 V and 750°C. The reactant utilization changed with the current during operation, starting from 38.5% and ending at 20.6%. Analysis of the impedance data was performed using the software Rادیoreal. Post-test analysis of the cells was performed using scanning electron microscopy (SEM). Polished cross-sections along the hydrogen/steam flow path from inlet to outlet were prepared for all the cells. The cell microstructure was examined using a Supra-35 scanning electron microscope equipped with a field emission gun (FE-SEM, Carl Zeiss) and an energy-dispersive X-ray spectrometer (EDS, Thermo Electron Corporation). For SEM imaging, low voltage (LV) SEM through lens detector and an accelerating voltage of 1 keV was employed. The samples were embedded in epoxy and carbon coated to avoid charging of the sample surface and to ensure a grounded connection. Fractured samples were prepared from hydrogen inlet to outlet and were carbon coated for analysis. In-lens and SE detectors were used at 5 keV to investigate the surface morphology of these samples.

Results and Discussion

Three SOA cells were characterized and the initial performance under the conditions for co-electrolysis i.e., 65% H₂O+25% CO₂+10% H₂, at fuel electrode with oxygen at the oxygen electrode at 750°C are compared in Figure 1. It was of interest to test cells at nominal temperature given by the supplier as well as aimed at by the project (EU-Eco). The OCV values are very similar to each other as well as to the theoretical value, indicating a tight setup. Cell C deviates from the other cells at higher current densities, and hence the operating point for long-term operation was chosen within the window where the cells exhibited more similar behavior. It is particularly of interest to operate the cell in potentiostatic mode and is desirable to operate the cell at thermostable voltage (1.33 V for the given gas composition). However, for the cells in this study, such an operating voltage would yield high current densities of approximately 1 A/cm² (See Figure 1), which may result in significant degradation. From the i-V curves shown in Figure 1, similar performance can be assumed while operating at 0.75 A/cm² for cells A and B, which corresponds to 1.2 V for Cell C. This operating voltage was therefore chosen for the potentiostatic test and the corresponding current density for the galvanostatic test. Cell A was used as reference for the micro structural analysis (see Figure 1).

Electrochemical Analysis

Cell B was tested galvanostatically at 0.75 A/cm² for 1050 hours. The evolution of cell voltage and current density can be seen in Figure 2a. The increase of cell voltage was fast in the initial 200 hours of operation with a degradation rate of 0.7 mV/h (58%/1000 h). Later on, during the durability test, there was a slower increase of the cell voltage. In the last 655 hours of operation, the degradation rate was 0.13 mV/h (10%/1000 h).

Cell C was tested potentiostatically at 1.2 V for 1005 hours and the evolution of the cell voltage and current density over the testing period can be seen in Figure 2b. Here, the initial current density at the start of durability test was lower than that of Cell B due to double headed arrow on Figure 2b. The polarization resistance of Cell C (potentiostatic test) was larger than in the case of Cell B (galvanostatic test) when the durability test was started (Figure 6), although the initial values should have been similar when looking at the first IV curves (Figure 1) that were the basis for the selection of operating current and voltage in these two tests. Obviously, Cell C had already experienced some degradation between this first IV curve and the starting IV curve of the durability test with the starting Rp almost double of the Cell B. Like in the case of galvanostatic testing, a rapid decrease of the current density was observed in the initial 200 h of testing which corresponds to a degradation rate of 17.2 mA/h (181%/1000 h). The decrease of current for the remainder of the test was much smaller, with a cell degradation rate of 1.3 mA/h (14%/1000 h) during the last 865 h of operation. In the initial 600 hours of durability testing, the cells degrade faster and the degradation rates typically decrease with increasing operation times. This behavior has been observed on different types of state-of-the-art cells.

Typically, degradation rates are given in change of cell voltage per 1000 h. Under potentiostatic conditions, the changing parameter is the current density and the degradation rate was therefore calculated as change of this parameter. However, these two parameters cannot be compared directly. To make a better comparison of the cell degradation in both modes of operation, area specific resistances (ASR) were
calculated using the following equation:

\[
\text{ASR} = \frac{(\text{OCV} - U)}{I}
\]  

where, OCV is the open circuit voltage determined through the Nernst equation, U is the cell voltage, and I is the current density.

The OCV value obtained just before starting the durability testing was used for ASR calculations. The OCV before and after the test were recorded as having the same values, for each cell, thus justifying using the initial OCV for ASR calculations. In Figure 3, the ASR values as calculated according to Equation 1 are plotted as a function of time, for both galvanostatic and potentiostatic test. From the slope of the ASR curves, it is evident that the cells degrade at a significantly higher rate during the first 200 h (right axis in Figure 3) of operation, as mentioned earlier in this work. After the initial 200 hours, the ASR increases with a slower rate until it becomes more stable. The ASR value increased with around 9%/1000 h for cell B tested under galvanostatic mode and around 14%/1000 h for cell C tested under potentiostatic mode during the first 200 hours. For the remainder of the testing time, the ASR evolution is similar in both modes, approximately 2%/1000 h. Thus, the observed trend for ASR degradation confirms the observations from following the cell voltage in galvanostatic mode and the current density in potentiostatic mode over time (see Figure 2). It allows though for a better direct comparison of the two operating modes, which under the applied conditions lead to similar overall degradation rates.

EIS were recorded under operation to achieve a more detailed understanding of the degradation processes within the SOFC. In Figure 4, Nyquist plots for Cell B under galvanostatic testing at 0.75 A/cm² are shown for selected operating times. It can be clearly seen that in the first 200 hours of operation the serial resistance (Rs) remained constant while Rp increased rapidly (twice as initial, compare also to Figure 6). During the remainder of the durability test, both Rs and Rp increased. In the last 200 hours, however, the increase of ASR of the whole cell is marginal and the cell seems to stabilize. In case of galvanostatic testing, gas conversion remained the same due to constant current density.

In Figure 5, similar plots for the cell impedance during the test at 1200 mV are plotted for Cell C. It is interesting to note that Rs remained constant over the whole testing period. Like in the case of galvanostatic testing, the increase of Rp was higher in the initial 200 hours. Rp doubled in the first 200 hours, as seen from Figure 5. In the last 200 hours, the polarization resistance increased only slightly suggesting a stabilization of the cell performance.

In order to get a more detailed information about the degradation mechanisms, the trends of serial (Rs) and polarization (Rp) resistances for the cells tested galvanostatically and potentiostatically were calculated from EIS under operation (see Figure 4). It should be noted that the polarization resistance for Cell C was significantly higher than that of Cell B at the start of durability test although initial values were similar as obtained from Figure 1. Cell C had already experienced certain degradation between this first IV curve (see Figure 1) and the starting of the durability test with the starting Rp almost double of the Cell B. In addition, cell-to-cell variation can be one of the reasons for the difference in polarization resistance. As indicated by broken lines in Figure 6, the behavior of both serial and polarization resistances is similar in both modes in the initial 200 hours; Rs remained constant while Rp displayed a rapid increase. In the initial 200 hours, similar degradation mechanisms are therefore suggested. After this initial period, the degradation of the cells shows different Rs and Rp trends under the different operating modes. For the galvanostatic test, Rs increased for the rest of the durability test while it remained constant for the potentiostatic test. A significant increase of Rs was previously
observed under conditions of high current densities/over potentials at the fuel electrode. From the results in the current study, it is suggested that running co-SOEC in potentiostatic mode seems to prevent this severe degradation mechanism from occurring because the current density is decreasing during testing below a critical value. In that way, the cell is “protected” from this specific degradation mechanism.

To analyze the change of the cell performance, i-V curves recorded before the beginning and after the end of durability testing are compared in Figure 7 and Figure 8. For Cell B, there is a clear change of the slope of the curves before and after testing (see Figure 7), representing an increase of the cell ASR. Regarding 1.3 V as the reference, before testing a current density of 0.95 A/cm² was observed while after the 1000 hours of testing, the current density significantly decreased to 0.6 A/cm². However, no fuel starvation is observed in the i-V curves, i.e. no bending of the i-V curve at high current density over the measured range.

In Figure 8, i-V curves before and after 1000 hours of Cell C under potentiostatic testing are plotted. After testing the degradation of the cell ASR is also significant. Taking 1.3 V as reference, at the start of the test a current density of 0.9 A/cm² was observed which decreased to 0.45 A/cm² at the end of durability testing.

To further identify the degradation mechanism pertaining to the individual electrodes, analysis of EIS spectra using distribution of relaxation times (DRT) was performed. To assign single electrode processes to a specific frequency or frequency range in the DRT, a gas shift analysis was done on both electrodes at OCV prior to and after the durability tests. To identify the processes related to the fuel electrode, change of the steam content at the fuel electrode was performed while keeping the gas on the oxygen electrode unchanged and the DRT plots were compared. Similarly, to identify the processes related to the oxygen electrode a change from oxygen to air was made while the fuel electrode gas composition was kept constant. These plots are displayed in Figure 9. DRT analysis is performed on the EIS measured
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Figure 7. i-V curves for Cell B before and after galvanostatic durability testing with 65%H_2O+25%CO_2+10%H_2 supplied to the fuel electrode compartment and O_2 supplied to the oxygen electrode compartment at 750°C.

Figure 8. i-V curves for Cell C before and after potentiostatic durability testing with 65%H_2O+25%CO_2+10%H_2 supplied to the fuel electrode compartment and O_2 supplied to the oxygen electrode compartment at 750°C.

Figure 9. DRT during initial fingerprint (OCV) for Cell C (a) temperature shift (b) fuel electrode gas shift (c) oxygen electrode gas shift.

on Cell C from the fingerprint. The behavior during initial fingerprint regarding gas shifts etc. was representative and comparable to Cell A and Cell B.

The relaxation times of the processes occurring at the SOA solid oxide cells are identified here including results from the literature studies performed previously [12,20,21]. A complete assignment to gas conversion, diffusion, and three phase boundary (TPB) processes was performed for the particular SOEC in this work. The processes along with their relaxation frequencies are listed in Table I.

Once the electrochemical contribution was identified, impedance spectra were compared for both operating modes (see Figure 10) before the beginning (labelled before in Figure 10b) and after the end (labelled after in Figure 10) of the durability test at OCV. Significant increase of resistances was observed indicating degradation of the cells under operation, thus confirming the results after the analysis of the i-V curves and the current/voltage trends during operation (see above).

The polarization resistances were further analyzed to identify the degradation of individual electrodes using DRT analysis.

Analyzing the polarization resistances through DRT plots in Figures 10a and 10b, both fuel and oxygen electrodes are seen to be degrading for both modes of operation. A shift in frequency of the processes was observed after long-term testing. The analysis is supported by EIS spectra analysis under current regarding the evolution of arcs. For the cell tested galvanostatically for 1000 hours, degradation is observed at the fuel electrode for both high frequency (1–10 kHz) and medium frequency process (100–1000 Hz). It is to be noted that medium frequency process has a contribution from the oxygen electrode as well. The DRT analysis shows an increase of processes for both electrodes by a factor of 3–4 (see processes 3 and 4 in Figure 10a), while the high frequency are (see process 5 in Figure 10a) itself increased by a factor of 4, approximately as compared to the initial ASR. Previous studies have indicated the loss of percolation of Ni network to be one of the major causes for the Ni-YSZ active electrode degradation. [13,15,30] This phenomenon will be investigated in the microstructural analysis. Additionally, in galvanostatic testing, an increase of Rs was also observed (see Figure 9), delamination of the layers is therefore suggested since this would affect both serial and polarization resistances. [13,1]

For the case of potentiostatic testing, it is obvious that the serial resistance remained constant, while the polarization resistance increased significantly. Further, DRT of the polarization resistance points toward both fuel electrode and oxygen electrode degradation at the frequency range of 500–1000 Hz. The increase of the ASR through DRT is in the order of 2–2.5 times the initial. The process 4 in Figure 10b degraded more significantly as compared to the test at galvanostatic conditions.

For some degradation mechanisms, electrode overpotentials were discussed as major parameter. [14] In this study the overpotential of the whole cell including the electrolyte was considered. The overpotential of the SOEC under durability testing was calculated for the tests in this study at:

\[ \Delta \eta = \frac{V - OCV}{2} \]

where, Op is the cell overpotential, V is the cell voltage, OCV is the open circuit voltage.

These values are displayed in Table II.

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Table I. Assignment of single electrode processes in the SOEC as a result of initial fingerprint EIS analysis using DRT.

<table>
<thead>
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<th>No. in Figure 9</th>
<th>Process</th>
<th>Relaxation frequency</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Gas conversion</td>
<td>1–3 kHz</td>
</tr>
<tr>
<td>2</td>
<td>Diffusion</td>
<td>30–50 Hz</td>
</tr>
<tr>
<td>3</td>
<td>Fuel and oxygen electrode</td>
<td>100–1000 Hz</td>
</tr>
<tr>
<td>4</td>
<td>Fuel and oxygen electrode, TPB processes</td>
<td>1–8 kHz</td>
</tr>
<tr>
<td>5</td>
<td>Fuel electrode, oxygen ion transport</td>
<td>18–30 kHz</td>
</tr>
</tbody>
</table>

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Figure 10. EIS and DRT before and after (a) galvanostatic testing, (b) potentiostatic testing at OCV with 65%H₂O+25%CO₂+10%H₂ supplied to the fuel electrode compartment and O₂ supplied to the oxygen electrode compartment at 750°C.

<table>
<thead>
<tr>
<th>Test</th>
<th>Overpotential at the beginning of test</th>
<th>Overpotential at the end of test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanostatic</td>
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<td>352 mV</td>
</tr>
<tr>
<td>Potentiostatic</td>
<td>329 mV</td>
<td>338 mV</td>
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</tbody>
</table>

Regardless of the difference of the current density at the beginning of the test in both modes, and thereby the ASR, the overpotential for both modes are comparable, as it was aimed at. For the galvanostatic test of Cell B, the overpotential for the cell increased by a magnitude of 250 mV. Interestingly, since the conversion arc remains constant, the overpotential can be clearly attributed to the electrode processes as displayed in Figure 10a. Both oxygen and fuel electrode contribute to the increase of overpotential. However, an extra contribution from the fuel electrode is seen at high frequency which can result from the increasing overpotential.

For the potentiostatic test of Cell C, the start and the end of the test have similar overpotential. This is as expected since the potential of the cell is kept constant in potentiostatic mode while the current density decreases over the time, from 0.59 A/cm² to 0.32 A/cm² over the 1000 hours of testing. The attribution of electrode contributions to the degradation is more complex than in the case of galvanostatic operation since the gas conversion is different at the start and end of the test. The DRT results indicate that both electrodes are degrading as seen from Figure 10b. The difference of degradation mechanisms compared to the galvanostatic test is seen by the high frequency attributed to the fuel electrode which is constant throughout the potentiostatic test.

**Microstructural Analysis**

To complement the electrochemical results, Cells A, B, and C were analyzed with the help of a Scanning Electron Microscope (SEM). The cells were investigated at 1 keV under In-lens detector to visualize the percolating Ni network. Pores, YSZ and non-percolating Ni are seen as dark particles in In-lens images, while percolated Ni particles appear as bright spots. Complementary Secondary electron (SE-2) images are also shown to better visualize the phases present in the samples.

By comparing the Ni particles in SE-2 images to that in the In-lens, the loss of percolation can be estimated.

In all SEM figures (Figure 11, Figure 12 and Figure 13), the oxygen electrode (LSFC-CGO) is on top, followed by the CGO barrier layer, the YSZ electrolyte and the Ni-YSZ active layer and support layer for the fuel electrode at the bottom. The bright particles shown in the
In-lens images are the percolating Ni particles, while the non-percolating (isolated) Ni particles appear to be dark.

When compared with the reference cell in Figure 11, Ni seems to percolate to a lesser degree in the galvanostatically tested cell (specified marker in Figure 12a). Fuel electrode degradation was concluded from the electrochemical analysis, which is thus confirmed by the percolation images taken from cell pieces at the gas outlet in Figure 12. A loss of active TPBs seems thus responsible for the observed degradation.12,13,15 The images are representative of the cell in general, even though only the image from the H2 outlet is shown. In addition, a gap is observed at the cell piece close to the gas outlet, at the interface of CCGO and YSZ layers in the SE-2 image clearly (see marker on Figure 12b). The delamination has occurred during testing (as there was an increase of the serial resistance) or in the post test preparations on spots that were weakened during the test.

In Figure 13, images were taken at cell pieces from fuel electrode outlet of the Cell C where it is clearly observed that the cell is cracked from oxygen electrode, through the inter-diffusion barrier layer, the electrolyte and into the active fuel electrode (see marker on Figure 13b). The contrast in phases is not clearly visible. However, looking at the complementary in-lens image (see marker Figure 13a) it is observed that the particles in the vicinity of the crack are no longer percolating, and it is probable that locally oxidation of Ni has taken place. To analyze the onset of cracks, OCV values are compared at the beginning and the end of the durability test. The OCV values were similar (see Figure 8) and therefore it is probable that the crack did not occur during the durability testing.

Once the durability test was completed, the cell was characterized with varying gas compositions on both fuel and oxygen electrode as described in the Experimental section prior to cooling down the cell. During this characterization, a sudden increase of ASR was observed along with a change in the temperature at high steam content of over 80%. We assume that the cracks started to appear from the active fuel electrode vertically through the cell from this point onwards. This further leads to a drop of OCV at high steam conditions and co-electrolysis when compared to the initial fingerprint. Hence, the cracks are not a consequence of the long-term test.

It was desirable to investigate the percolation of Ni particles in other parts of the cell, where the cell was not cracked completely, and the layers were in adhesion. In Figure 13c, percolation of Ni particles is observed through in-lens images at 1 keV. At the active fuel electrode at 20X magnification, the network of particles right next to the electrolyte (see top of the image) seem to be percolating. Hence, no considerable loss is observed adjacent to the electrolyte in the active fuel electrode. As mentioned earlier, Ni percolation is representative of the whole cell i.e., similar behavior was observed in different locations of the cell from H2 inlet to outlet.

In contrast to the observations after testing in oxygen electrode, no cracks along the YSZ/CCGO interface were observed after the potentiostatic test, which is in line with the constant serial resistance over time as seen from the EIS.

Conclusions

Two SCa cells were tested for durability in galvanostatic and potentiostatic modes for a comparison of the degradation mechanisms during co-electrolysis of steam and CO2. The overall degradation behavior similarly. There was a faster initial degradation of both cells' ASR in the initial 200 h followed by a period of slower degradation over the later ca. 800 h of operation. EIS characterization of the cells before and after test showed a degradation of both electrodes. EIS measurements during operation support this finding. A similar behavior of the polarization and the serial resistance occurred in the initial 200 hours with increase of 0.1 Rp in both modes, while Rs remained constant. This suggests similar degradation mechanisms. The degradation continued differently after this initial period. In the remaining testing hours, both Rs and Rp increased in the galvanostatic mode while only Rp increased in the potentiostatic mode. The reason for these different long-term degradation mechanisms can be due to the different trends of overpotential over time. While at the start of both tests the overpotentials were similar, the overpotential increased over the time in the galvanostatic mode as the current density was kept constant. On the other hand, the overpotential remained constant in the potentiostatic mode because the voltage was kept constant. Thus, overpotential related degradation mechanisms will not occur to the same extent as in galvanostatic mode. This is also evident from the increase of the high frequency attributed to the fuel electrode, which was only observed in the galvanostatic test. In the potentiostatic mode the cell is obviously protected by automatically lowering the current density in the course of degradation and does not reach the critical value for the threshold of such an electrochemical degradation process related to the respective electrodes. SEM analysis indicates loss of percolation of the Ni network at the active fuel electrode in the galvanostatic mode. The study has shown that operating a SCa cell in potentiostatic mode in co-electrolysis is an interesting mode to prevent some causes for degradation.

Acknowledgments

The author wishes to thank H. Henrikss, M. Davodi, Dr. J. Bentzon and Dr. K. Thysen for their technical help with measurement and testing. The research leading to these results has received funding from the European Union’s Horizon 2020 framework program (H2020) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement no. 669092 (“Efficient Co-Electrolyser for Efficient Renewable Energy Storage-ECO”).

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References


Unwinding Entangled Degradation Mechanisms in Solid Oxide Electrolysis Cells Through Electrode Modifications and Impedance Analysis
Unwinding Entangled Degradation Mechanisms in Solid Oxide Electrolysis Cells Through Electrode Modifications and Impedance Analysis

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Received December 11, 2018; accepted May 23, 2019; published online.

Abstract
In the renewable energy scenario, energy storage is of essence. In this context, Power-to-Liquid (PtL) and Power-to-Gas (PtG) concepts have attracted large attention, where the use of solid oxide electrolysis cells (SOECs) has a huge potential, due to their high conversion efficiencies. However, performance and durability of these cells still need to be improved for a large-scale commercialization of the SOEC technology. It is often difficult to identify the various loss and degradation mechanisms limiting the cell performance and durability. This paper contributes to this scientific discussion, by providing a careful analysis of the degradation mechanisms occurring in three different cells during long-term H2O and CO2 co-electrolysis, at 1,200 mV. Electrochemical impedance spectroscopy (EIS) is measured before, during and after the electrolysis operation, and is utilized to address the individual electrode degradation mechanisms and the development of leaks through the electrolyte. Moreover, the leak rates under open circuit voltage (OCV) measurements were compared. In addition, microstructural analysis of the electrodes and electrolyte is related to the electrochemical findings to contribute to the discussion on the interdependency of the degradation mechanisms.

Keywords: Co-electrolysis, Distribution of Relaxation Times, Durability, Electrochemical Impedance Spectroscopy, Infiltration, Nickel Migration, Percolation, Potentiostatic, Solid Oxide Electrolysis Cell

1 Introduction
Renewable energy sources are gaining importance for energy production worldwide. For instance, in the case of Denmark, almost 50% of electricity production currently is provided through wind turbines and is expected to transition towards 100% by 2050 [1]. Due to the intermittency of renewable energy sources such as solar and wind, storage of electricity is of essence. Furthermore, there is an increasing need for production of renewable fuels for the transport sector. In this context, SOECs can play a major role for PtG and PtL applications, by the means of co-electrolysis of H2O and CO2 to synthetic gas (H2 + CO), and further on to hydrocarbons [2–7].

One of the promising scenarios is to use SOECs for methane production, which can be stored and distributed in the existing natural gas infrastructure [8].

However, the performance and durability of SOECs need to be improved further, to realize a successful commercialization [7, 9–12]. Satisfying durability is, in particular, a challenge if the cells are operated at high current density [13]. SOECs, in this work, refer to the fuel electrode supported cell configuration. Degradation of the cermet of Nickel and Yttria Stabilized Zirconia (Ni:YSZ) active layer, is typically related to microstructural changes such as coarsening of Ni particles, migration of Ni particles away from fuel electrode adjacent to the electrolyte, decrease in the Ni:YSZ contact area, and loss of...
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percolation of Ni particles [14]. The irreversible microstructural degradation during the long-term tests might relate to the impurities in the gas stream [15,16]. Another contributor to the area specific resistance (ASR) of the cell is the oxygen electrode, through the oxygen electrode activity [17,18]. A vast number of routes to address these challenges are currently being investigated [19]. This includes improvement of the oxygen electrode through backbone infiltration [20,21], and optimization of the particle size, porosity and percolation in the Ni-YSZ electrodes [10].

In this work, a state-of-the-art (SoA) cell (Cell-A) was tested as a reference. The work performed in this study was to enhance the performance of this SoA cell. This was done by modifications of the electrodes and resulted in Cell B and C. Two modified cells comprising of (i) a cell with a gadolinium doped ceria (CGO) oxygen electrode backbone structure with lanthanum strontium cobaltite (LSC) infiltrated into the backbone (Cell-B) and, (ii) a cell with modified fuel electrode structure and an LSC-CGO composite oxygen electrode (Cell-C), were tested for initial performance and long-term durability in co-electrolysis mode, and compared to Cell-A. This work analyzes the electrochemical performance of the cells and compares the impact of the electrode modifications.

2 Experimental

Three different types of SOECs were tested in this study, as shown in Figure 1.

Cell-A, a state-of-the-art cell, is used as a reference cell. It has a 40-60 µm lanthanum strontium cobaltite (LSC)/CGO oxygen electrode, a CGO barrier layer, a 6-10 µm thick YSZ electrolyte, and a 220-260 µm thick Ni-YSZ fuel electrode, which also serves as a support layer. Cell-B has a 30 µm thick CGO backbone layer in which LSC was infiltrated, a 6-7 µm thick CGO barrier layer, a 10 µm thick YSZ electrolyte, a 12-15 µm thick Ni-YSZ fuel electrode, and a 300 µm thick Ni-YSZ support layer. For infiltration of LSC into the CGO backbone, 5M solution of LSC was used, and the cell was heat treated at 580°C after infiltration. This procedure was repeated 9 times to establish sufficient LSC solid loading in the CGO backbone. Cell-C has a 30 µm thick composite LSC- CGO oxygen electrode, similar barrier layer, electrolyte and support as Cell-B, and a fuel electrode optimized by densifying the fuel electrode to obtain 22% porosity after NiO reduction. The cell fabrication method is published elsewhere [10]. The active area of the cells was 16 cm².

The cells were tested in a previously described test setup [22, 23]. They were mounted on an alumina cell test house with gold and nickel as current collector contact components on the oxygen and fuel side, respectively. A gold sealing was used on the fuel side: 4 kg of weight was applied on top of the cell house during start up to ensure gas tight sealants and electrical contact between the cell and the contact components. Cell-A was heated to 800°C at a ramp rate of 60°C/h and held for 2 h prior to reduction. During heating, N₂ and air were supplied to the fuel electrode and oxygen electrode compartment, respectively. The cell was reduced with N₂ and H₂ beginning from 90% N₂, for 1 h, eventually shifting the flow to pure H₂ for 1 h on the fuel electrode. Cell-B and Cell-C were heated to 850°C at a ramp rate of 60°C/h and held for 2 h prior to reduction. During reduction, a mixture of 9% H₂ in N₂ was supplied to the fuel electrode. Cell-A is a commercial SoA cell while Brand-C are produced in-house. Cell-A is reduced at 800°C as per manufacturer's protocol and the other two cells made in-house need to be reduced at 850°C. In order to achieve best performance and durability, the cells need to be reduced at the optimized temperature for the specific cell types. On the oxygen electrode, a constant air flow of 140 normal liter per hour was maintained. Initial electrochemical characterization (fingerprint) of the cell was performed afterwards.

The fingerprint is a standardized electrochemical characterization of the cells at 800°C, 750°C, 700°C and 650°C. At each temperature, J-V characterization and EIS measurements were performed with air or O₂ supplied to the oxygen electrode, and with 4%, 20%, 50%, 80%, or 90% steam in H₂ to the fuel electrode. Furthermore, characterization in co-electrolysis gas mixture was carried out with 45% H₂O + 45% CO₂ + 10% H₂ or 65% H₂O + 25% CO₂ + 10% H₂ supplied to the fuel electrode.

EIS measurements during fingerprint were carried out at OCV condition, using a Solartron 1255 frequency analyzer and an external shunt resistor in series with the cell. The spectra were recorded from 96,850 to 0.08 Hz, with 12 points per decade, and were corrected using the short circuit impedance response of the test setup. A short-circuit impedance response for compensation of EIS was measured without the cell test house. From the impedance spectra, the ohmic resistance of the cell (serial resistance, Rs) was taken as the value of the real part of the impedance at 96,850 Hz. Conventionally, the Rs is obtained from the intercept of the Z'-axis. However, as previously reported by Sun et al. [7], the calculation of Rs performed in this work provides a more precise value. The difference between the
intercept and this value is indeed very small. The polarization resistance ($R_p$) was then calculated as the difference of the real part of the impedance at 96,850 Hz and 0.08 Hz. EIS measurements during durability tests were carried out at 1.2 V. 

$I-V$ curves were recorded both in fuel cell (FC) and electrolysis (EC) mode with the above-mentioned gas compositions. For FC mode, the minimum voltage limit was set to 650 mV while for EC mode the curve maximum voltage was set to 1,300 mV. The $I-V$ curves were recorded in 3 parts with step sizes of firstly 0.25 A, followed by 0.5 A in the linear region, and finally 0.25 A. The step size of 0.25 A was maintained, until either the current or voltage threshold was reached.

The electrochemical durability testing of the cells was carried out at 750°C in co-electrolysis mode with 65% $\text{H}_2\text{O}$ + 25% $\text{CO}_2$ + 10% $\text{H}_2$ in the fuel feed corresponding to a theoretical thermodynamic equilibrium composition of 23% $\text{CO}_2$ + 2% $\text{CO}$ + 8% $\text{H}_2$ + 67% $\text{H}_2\text{O}$. The voltage was kept constant at 1.2 V, with varying current densities throughout the durability testing, as a consequence of degradation [24]. Cell A and Cell C were tested for 1,000 h, while Cell B for 500 h. Analysis of the impedance data was performed using the software Radvad [25]. The overall test sequence is presented in Figure 2.

Post-test analysis of the cells was performed using scanning electron microscopy (SEM). Polished cross-sections along the hydrogen/steam flow path from inlet to outlet were prepared for all cells. The cell microstructure was examined using a Supra-35 SEM equipped with a field emission gun (FE-SEM, Carl Zeiss) and an energy-dispersive X-ray spectrometer (EDS, Thermo Electron Corporation). For SEM imaging, low voltage (LV) SEM through an In-lens detector at an accelerating voltage of 1 kV was employed [26]. The samples were embedded in epoxy and carbon coated to avoid charging of the sample surface and to ensure a grounded connection. Fractured samples were prepared from hydrogen inlet to outlet and were carbon coated for analysis. In-lens and SE detectors were used at 5 kV to investigate the surface morphology of these samples. EDS analysis was carried out at 10 keV for elemental analysis.

3 Results and Discussion

3.1 Overview of Electrochemical Performance

The three cells were characterized, and their initial performance was compared in Figure 3 under co-electrolysis conditions, with 65% $\text{H}_2\text{O}$ + 25% $\text{CO}_2$ + 10% $\text{H}_2$ to the fuel electrode and $\text{O}_2$ to the oxygen electrode, at 750°C. Cell A: S5A, Cell B: Cell with modified oxygen electrode, Cell C: Cell with modified fuel electrode.

![Fig. 3 I-V curves during initial characterization under co-electrolysis conditions with 65% $\text{H}_2\text{O}$ + 25% $\text{CO}_2$ + 10% $\text{H}_2$ to fuel electrode and $\text{O}_2$ to oxygen electrode, at 750°C. Cell A: S5A, Cell B: Cell with modified oxygen electrode, Cell C: Cell with modified fuel electrode.](image)

and $\text{O}_2$ to the oxygen electrode, at 750°C. The OCV values for the cells are similar, however they deviate from the theoretical value, in the range of 1–4 V. This indicates the presence of leaks in the test, which will be addressed later in this work.

Taking the Cell-A as reference, Cell-C performed better while Cell-B performed worse as can be seen from Figure 3. Cell-A and Cell-B performed similarly at low current densities, up to 0.2 A cm$^{-2}$. Thereafter, the performance of Cell-B deviated from Cell-A. Cell-C performed significantly better than the other two cells from the beginning. By modifying the oxygen electrode using the backbone/infiltration concept, a decrease of initial performance was observed, while by modifying the fuel electrode in terms of structure, a significant increase of performance was observed.

Owing to the difference in initial performance, the operational parameters for testing of long-term durability were determined. The selection of testing conditions was based on the project goals of the EU-ECO project: cells were tested at 1,200 mV and 750°C under co-electrolysis conditions. The overpotentials of the cells under durability testing were calculated for the tests in this study as [11]:

$$\text{Op} = U - \text{OCV} - I \times R_s$$

where $\text{Op}$ is the cell overpotential, $U$ is the cell voltage, OCV is the open circuit voltage, $I$ is the current density and $R_s$ is the serial resistance.

In this calculation, the contribution from the serial resistance is excluded to analyze the overpotential of only the electrodes. At an operating voltage of 1,200 mV, current densities of 0.6 A cm$^{-2}$ for Cell-A, 0.33 A cm$^{-2}$ for Cell-B and 0.8 A cm$^{-2}$ for Cell-C were obtained from the I-V curves. Following this, Rs and OCV (including leaks) were obtained, and the overpotential of the electrodes thus obtained are displayed in Table 1. The cells experienced similar electrode overpotentials. Furthermore, the long-term operation was carried out under potentiostatic conditions, and the overpotentials are similar at the beginning and end of this testing period.

In Figure 4a, the evolution of current density during the long-term tests is shown. Note, that a degradation under
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Table 1 Overpotential at the beginning and end of durability testing.

<table>
<thead>
<tr>
<th>Test</th>
<th>Rs at the beginning of the long-term test / Ω cm²</th>
<th>Overpotential at the beginning of the long-term test</th>
<th>Rs at the end of the long-term test / Ω cm²</th>
<th>Overpotential at the end of the long-term test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell-A</td>
<td>0.154</td>
<td>329 mV</td>
<td>0.157</td>
<td>324 mV</td>
</tr>
<tr>
<td>Cell-B</td>
<td>0.198</td>
<td>317 mV</td>
<td>0.208</td>
<td>313 mV</td>
</tr>
<tr>
<td>Cell-C</td>
<td>0.134</td>
<td>321 mV</td>
<td>0.131</td>
<td>318 mV</td>
</tr>
</tbody>
</table>

where OCV is the open circuit voltage measured experimentally, \( U \) is the measured cell voltage, and \( I \) is the measured current density.

The OCV used for ASR calculation is the one measured prior to the long-term test. This OCV change will be further discussed, in relation to the results on changes in electrode microstructure and resistance.

The ASR evolution for the cells is shown in Figure 4b. The general trends are comparable to those observed with the current density. Regardless of the difference in the initial ASR values, Cell-A and Cell-B show similar degradation behavior. In the first 200 h, a high rate of degradation of ASR is observed followed by a more gradual/stable lowering of the rate of degradation. For Cell-C, a different trend is observed which is more linear in nature and the overall rate of degradation is smaller than the other two cells. The high initial degradation of SOA cells was significantly reduced in this manner and the overall degradation rate as well. The high initial degradation of Cell-A was reduced due to difference in the cell structure with regard to modification done for Cell-C and the overall degradation rate as well. It should be taken into account that the initial ASR for Cell-C was the lowest amongst the cells, therefore Cell-C was exposed to a significantly higher current density at the beginning of the test, which might affect the degradation mechanisms as well. The ASR is calculated using the measured OCV values, which is different among the cells. However, the aim of this work is to determine the change in ASR to understand the underlying mechanisms clearly. As a change of ASR can be used as an indicator which can be analyzed relatively before and after durability test, the mechanisms can be deconvoluted.

Following the ASR and EIS evolution during testing, the behavior of serial (Rs) and polarization (Rp) resistances was investigated in more detail, because the cells displayed different degradation behavior. Previous studies have used normalized Rp vs. Rs plots to identify degradation mechanisms, e.g., Gazzani and Kesler [27]. In such a way, phenomena like delamination of layers or structural degradation can be distinguished. Figure 5 shows the Rp vs. Rs plots for the cells in this study. A vertical line from point (1,1) is a result of the dominance of Rp changes as compared to Rs, which might be caused by structural changes in the electrodes such as nickel coarsening, chromium poisoning and/or changes due to steam content on the oxygen electrode [28]. A horizontal line from point (1,1) shows the dominance of increase of Rs over Rp, for instance due to oxide layer growth. If the values follow the 45° slope, a loss of active area is indicated [28]. For Cell-A, the values seem to increase vertically from point (1,1) indicating only Rp increase, while for Cell-B both increase: Rp and to a certain extent also Rp in combination with Rs as seen from Figure 5. This is an indication of at least two different degradation mechanisms. For Cell-C, the plot follows the 45° slope, i.e., a parallel increase of Rs and Rp happens, indicating one...
dominant degradation mechanism, but a different one from Cell A. This gives an indication of different degradation mechanisms occurring in the cells. These findings will be further investigated using EIS results.

3.2 Electrochemical Impedance Analysis

To investigate the evolution of the cell performance during long-term testing, the impedance spectra are plotted with increasing time in Figure 6 for all three cells. In Figure 6a, the evolution of impedance from 0 h to 1,000 h is plotted every 200 h for Cell A. It is evident that there is no change in the serial resistance ($R_s$) while the polarization resistance ($R_p$) keeps increasing. However, it should be noted that the current density is not constant throughout the test, and a direct comparison of degradation mechanisms is not possible due to the change of the contribution of the gas conversion resistance as consequence of the changing current density. For the case of Cell B in Figure 6b, similar influence on $R_s$ and $R_p$ are observed. In addition, a small increase of $R_s$ occurred as seen from Table 1 and Figure 5. For Cell C, the evolution of EIS over time shows a completely different trend than the other two cells as shown in Figure 6c. An increase in $R_s$ is observed which might be due to electrode degradation cracks in the electrolyte. Furthermore, $R_p$ is increasing to a certain extent. The increase in $R_s$ can also be confirmed from the values given in Table 1. In total, the increase of impedance is smaller as compared to Cell A and Cell B which is in line with the observation of the other parameters discussed above.

To further identify the source and extent of degradation, specific degradation mechanisms need to be investigated. This was done by using distribution of relaxation times (DRT) from EIS spectra [25]. From DRT analysis, contribution of individual electrodes is deduced. This is done by gas shift analysis, where EIS are recorded in differently composed gas mixtures to oxygen and fuel electrodes at OCV. By varying the steam content, while keeping the gas to the oxygen electrode constant, the response of the fuel electrode is distinguished in the EIS spectrum, at a specific frequency range. Similarly, while keeping the fuel flow/composition unchanged, and by changing only the oxygen partial pressure (shifting from oxygen to air), the response of the oxygen electrode is noted. The characteristic frequencies identified by DRT for the individual electrode processes are given in Table 2.

For Cell A there is an overlap of electrode response for both fuel and oxygen electrode and hence the change of DRT for the individual electrodes was difficult to obtain. For Cell B and Cell C, the deceleration of arcs with respect to the contribution from individual electrodes was possible. However, to strengthen the identification, the DRT was also analyzed prior to the durability testing when the current was ramped up and down, respectively, to better resolve the electrode contributions. Furthermore, during and after the test, DRT analysis also rendered useful information. DRT plots are displayed for each cell from beginning until the end of the whole test in Figures 7a–7b, based on the characterization sequence illustrated in Figure 2.

In Figure 7, the responses of individual electrodes for Cell A are mapped over the whole test. DRT analysis during the initial fingerprint is not sufficiently resolved to distinguish the contributions of fuel and oxygen electrodes, as seen in Figures 7a and 7b. There is an overlap in the frequency of these pro-
Table 2: Identification of electrode processes through DRT gas shift analysis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Relaxation frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cell-A</td>
</tr>
<tr>
<td>Gas conversion</td>
<td>1-1.5 Hz</td>
</tr>
<tr>
<td>Diffusion</td>
<td>30-50 Hz</td>
</tr>
<tr>
<td>Oxygen electrode</td>
<td>100-1,000 Hz, 1-8 kHz</td>
</tr>
<tr>
<td>Fuel electrode, TBP processes</td>
<td>100-1,000 Hz, 1-8 kHz</td>
</tr>
<tr>
<td>Fuel electrode, oxygen ion transport</td>
<td>18-20 kHz</td>
</tr>
</tbody>
</table>

Processes from 100 Hz–8 kHz, as reported earlier [30]. There is an additional response from a fuel electrode process, at approximately 10–20 kHz. However, it is interesting to see the trend of degradation with ramping up of current. These two processes seem to move towards decreasing frequency, as seen from Figure 7c. Moreover, during long-term testing, the two processes seem to merge, and are seen in the form of a single arc in DRT spectrum shown in Figure 7d. This indicates that both the electrodes degrade over time. Furthermore, during the ramping down of current after the durability test as shown in Figure 7e, the processes can be seen separated at low frequency, but the summit frequencies have decreased. It was of interest to deconvolute the mechanisms after the long-term testing. DRT plots for fuel and oxygen electrode shifts are plotted with respect to the final fingerprint in Figures 7f and 7g. The two processes appear to overlap around 500 Hz. However, the contribution from the oxygen electrode has increased significantly as compared to the initial fingerprint, while the fuel electrode contribution increased slightly from the initial fingerprint. The magnitude of degradation of oxygen electrode is quite high as compared to the fuel electrode, which becomes obvious through the gas shift plots performed before and after the long-term test. This also indicates the presence of leaks. Regardless of the overlap of the frequencies, major contributions to the cell degradation is therefore attributed to the oxygen electrode ASR.

Similarly, the DRT plots for Cell-C are represented in Figure 8. Through initial fingerprint from Figures 8a and 8b, the deconvolution of individual electrode processes was possible with fuel electrode processes occurring at frequencies of 3–5 kHz and 10–20 kHz, while the oxygen electrode process was approximately around 500–1,500 Hz. During ramping-up of current in Figure 8c, the processes seem to move towards low frequency. Moreover, a clear distinction of the oxygen electrode process is seen under current. During the long-term test, the oxygen electrode degrades continuously, while the fuel electrode degradation is clearly visible until 400 h, in Figure 8d. The magnitude of degradation of oxygen electrode is significantly higher than the fuel electrode. This may be due...
to the non-optimized infiltration process of the CGO backbone with LSC solution, which has been further identified through SEM analysis. During ramping down of current as well as the final fingerprint, the deconvolution of arcs at OCV becomes difficult, as seen from Figures 8c, 8f, and 8g. This might be due to the severe degradation of the cell. Moreover, leaks were also present during the testing.

For the case of Cell-C, DRT plots are represented in Figure 9. Using initial fingerprint in Figures 9a and 9b, the response of oxygen electrode process is found around 180-200 kHz, while the fuel electrode processes occur around 1-3 kHz and 8-10 kHz. During ramp up of current, a shift towards lower frequencies is seen for the fuel electrode processes in Figure 9c. However, the conversion are present at approximately 1 Hz dominates the DRT spectrum and the electrode processes are not clearly stable i.e., the arc at 1 Hz is significantly larger in magnitude around 0.4 Ω cm² while the processes have a magnitude of approximately 0.05 Ω cm². During long-term testing, an increase in fuel electrode response is visible in Figure 9d. Furthermore, during ramping down of current as shown in Figure 9e, a similar trend is observed as in ramping up of current as seen from Figure 9c; however, the magnitudes of the fuel electrode response has increased. Moreover, from the final fingerprint, deconvolution of fuel and oxygen electrode processes is difficult indicating the cell degradation and increase in leaks.

From the DRT analysis over the whole testing period, Cell-A and Cell-B seem to degrade mainly due to the oxygen electrode. For explaining the degradation mechanisms, it is valuable to distinguish between the total overpotentials and the overpotentials experienced by the single electrodes. Even though the total overpotentials of the different cells might be similar, the distribution between the electrodes can differ and thus cause different degradation mechanisms. From Figures 7g and 8g, the DRT shows the magnitude of oxygen electrode response which is twice for the case of Cell-B when compared to Cell-A. The overpotential experienced by oxygen electrode in Cell-B is higher than that of Cell-A; hence, lowering the performance of Cell-B. For the case of Cell-C, the oxygen electrode is reasonably good and the overpotential experienced by the fuel electrode is higher than in the other two cells. This leads to a different degradation trend as revealed through electrochemical analysis.

To further emphasize on the leaks during testing, OCV values were used. The difference in OCV between the theoretical and measured value was related to the excess O₂ gas leak into the fuel stream. The calculated difference in leaks indicate the extent of growth of leaks leading to cracks/delamination, if any. Note: All flows are in NLM/h. To calculate the leak current, following equations are used:

\[ \text{Number of moles} = \frac{\text{excess } O_2 \text{ (L/h)}}{22.4} \]  

\[ \text{Leak current} = \frac{\text{Number of moles (mol/h) } \times (A \text{ s/mol})}{3,600 \times 16 \text{ cm}^2} \]
where $F$ is the Faraday constant, and $4$ refers to the number of electrons per mole of excess $O_2$ gas.

It can be seen from Table 3 that the leaks change significantly for Cell-B and Cell-C during testing. Cell-C is of special interest because this cell was operated at significantly higher current densities than the other two cells. The difference of measured to theoretic $OCV$ changed by 10 mV during the test.

As a result, the overpotential experienced by the fuel electrode will be even higher if no leaks were present. If the cell had no leaks, the $OCV$ measured would be higher leading to difference between operating potential and $OCV$ being lower. The impact of leak on Cell-C degradation and increase in $R_s$ will be further addressed through microstructural analysis, in the later part of this work. In addition, further information is given in Appendix A.

### 3.3 Microstructural Analysis

Once the electrochemical test was completed, SEM analysis was performed to investigate structural changes and correlate them to the electrochemical results. The cells were investigated at 5 kV and used for morphological (oxygen electrode) using a SE-2 detector and at 1 kV for pellet studies [26] (fuel electrode) using the Inels detector. In Figure 10, Cell-A, Cell-B and Cell-C are first compared to highlight the difference in the oxygen electrode structure. The oxygen electrode is on top, followed by the CGO barrier layer and the electrolyte. Cell-A consists of a composite LSCF-CGO oxygen electrode while Cell-B is prepared by infiltrating LSC solution into a CGO backbone and Cell-C consists of a composite LSC-CGO structure. Cell-A exhibits uniform particle size distribution throughout the electrode as seen from Figure 10a. For Cell-B, the areas adjacent to the CGO backbone show islands of LSC infiltrate instead of a continuous network of LSC nanoparticles as shown in Figure 11b. This indicates non-optimized infiltration. The non-optimized infiltration refers to the fact that a continuous network from the barrier layer to the oxygen electrode is considered to deliver high activity and thus a low area specific resistance. Instead, islands of infiltrates were observed. Such islands were also seen in a reference cell (sister cell to Cell-B), leading to the conclusion that the infiltrates were not forming a continuous network. This is displayed in Figure 11c. This results in higher ASR for the whole cell and lower performance. Cell-C consists of composite LSCF-CGO oxygen electrode.

### Table 3 Calculation of leaks in the cell setup ($50\% H_2 + 50\% H_2O$ at the fuel electrode, $O_2$ at the oxygen electrode, at 750 °C)

<table>
<thead>
<tr>
<th>Cell</th>
<th>Difference in $OCV$ before</th>
<th>Difference in $OCV$ after</th>
<th>Corresponding $leak$ current before</th>
<th>Corresponding $leak$ current after</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell-A</td>
<td>25</td>
<td>25</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Cell-B</td>
<td>6</td>
<td>12</td>
<td>45</td>
<td>67</td>
</tr>
<tr>
<td>Cell-C</td>
<td>12</td>
<td>23</td>
<td>67</td>
<td>90</td>
</tr>
</tbody>
</table>
An interesting aspect while comparing Cell-B and Cell-C relates to the CGO backbone for Cell-B, which seems to be very porous while the composite structure in Cell-C is denser. For Cell-B, even though there might be LSC particles surrounding the CGO backbone, the overall network of active sites is reduced as compared to Cell-C. This is further seen in Figure 11. Here, the images are taken at high magnification to assert the importance of combination of backbone and infiltration on the cell performance. LSC particles are clearly visible locally, for example indicated by the red circle in Figure 11b. However, the structure seems too coarse for the oxide ion conduction. This implies that there are infiltrates present around CGO backbone locally; however, the backbone itself is too coarse and the conduction path for the ions is reduced in this manner. The results indicate the inferior percolating capacity of the infiltrates for Cell-B. The infiltration technique can be further optimized to improve the performance of the cell. As a conclusion, the oxygen electrode structure overall is significantly inferior to Cell-A and Cell-C.

The other modification concept, fuel electrode improvement is investigated next. In Figure 12, the cells are compared such that the electrolyte is on top followed by the fuel electrode active layer and support. Moreover, bright particles in the fuel electrode represent percolating Ni [26]. Clearly, there is a significant difference in the porosity and particle size distribution for all three cells. For Cell-A, there is a uniform densely packed fuel electrode while for Cell-B and Cell-C, only the active layer is densely packed, but being more porous than Cell-A. For Cell-A and Cell-B, given that the cells operated at lower current density, the Ni network seems to be still percolating to a good extent. In Figure 12a, the fuel electrode of Cell-A shows a good percolation (bright spots towards the dark electrolyte) with a rather densely connected Ni network. During testing of Cell-A, cracks were observed only in post-mortem analysis. This has been investigated previously [30], wherein it was concluded that the cracks were not formed during the long-term testing, but afterwards. No change in OCV or Rs was observed during testing in this study, indicating that the cracks indeed were formed during final characterization. In Figure 12b, the same region also shows good percolation of Ni particles. In Figure 12c, percolated Ni particles of Cell-C are less in number when compared to Cell-B in the active layer. The loss of percolation as a result of higher overpotential experienced by the cell is indicated.

To further assess the different effects of the fuel electrode overpotential for Cell-B and Cell-C, owing to their similar half-cell structure, the tested cells after long-term testing are
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Fig. 12 SEM images at 1 keV for fuel electrode comparison (a) Cell-A with YSZ electrolyte on top, followed by Ni-YSZ electrode; (b) Cell-B; and (c) Cell-C, with YSZ electrolyte on top, followed by Ni-YSZ active electrode and support; cells after testing.

compared to sister cells on which only fingerprint was performed. These are displayed in Figure 13. Loss in the Ni network is observed close to the electrolyte layer for Cell-B, as seen from the yellow circle in Figure 13a. For Cell-C, after long-term testing at higher current densities than the other two cells, the loss of Ni percolation reaches a large extent. It is visible that Cell-C has lost significant amount of percolating Nickel after long-term test from Figure 13b, which is not the case for Cell-B.

It is interesting to recall that the Rs of Cell-C gradually increases over time. Moreover, this cell had the highest leak current amongst the three cells tested for durability. The change in Rs can be attributed to the loss of active area. To address this aspect, the microstructure of the cell with special emphasis on the electrolyte layer was investigated.

The delamination of the electrolyte layer is clearly visible in Figure 14. Grain boundary deterioration is observed in the electrolyte which indicates the weakening of interfaces due to high overpotential experienced by the cell, which is seen in post-mortem analysis.

It is difficult to conclude the extent of influence of Ni migration or crack formation on the increase in Rs. Loss of percolation indicated the Nickel migration from the active layer to the support. Hence, it was also of interest to investigate the theory of Nickel migration [31]. For this purpose, line scans were done through Cell-C to check for the possibility of loss in Ni surface area due to migration. Figure 15 displays the difference in Ni content at the inlet, middle, and the outlet of the reference cell (tested only for fingerprint) and the long-term tested cell. To obtain these plots, EDS line scan was performed close to the electrolyte in the active fuel electrode as well as in the support layer near the active fuel electrode. The schematic representation is displayed in Figure 15a. The distance for the line scan is denoted in μm, with the distance being taken such that the interface between electrolyte and active fuel electrode is the reference. Inner active line scan was taken 1–2 μm from this interface, along with outer active line scan being taken at 7–8 μm from this interface and the support line scan being taken at 12–15 μm from this interface. Therefore, the counts are summed up and averaged. For further information, please refer to Appendix B. This methodology gives an indication of the magnitude of the Ni migration from the active region to the fuel support [31].

From Figure 13b, the inlet displays a lack of Nickel in the inner active electrode layer (i.e., at the electrode/electrolyte interface) while the outer layer as well as the electrode support display similar ratio of Ni/(Ni+YSZ), taking into account the
Fig. 15 (a) Schematic for EDS scan positions. Graphs displaying amount of Nickel in long-term tested cell, CellC (red circle) as compared to the reference cell, sister cell to CellC (blue diamond) at (b) inlet, (c) middle, and (d) outlet of the cell, with respect to the fuel flow direction (the double headed arrows indicate the error bar, i.e., the margin of error in analysis).

error bar for the data analysis. However, for the case of middle and outlet of the cell the counts are almost similar in both reference and the long-term tested cell within the margin of error. This explains qualitatively that Ni migration occurs predominantly at the inlet of the cell, where also the highest humidity is observed. Humidity has been reported earlier to favor the migration of Ni [31]. This asserts the fact that for Cell-C, degradation is due to Ni migration and resulting loss of percolation. Moreover, change in Rs is a result of Ni migration as reported by Mogons et al. [31]. Due to testing conditions, the deterioration of electrolyte and interfaces take place, leading to crack formation and increase in leaks. Further, crack formation due to leaks also causes an increase in Rs, which has been reported earlier [17].

4 Conclusions

The aim of the study was to reveal the different degradation behavior of the cells operated under co-electrolysis conditions with modified electrodes for durability at potentialistic mode of operation and compare the performances with the SnA cell. Two concepts were investigated, namely (i) oxygen electrode modification by infiltrating LSC solution into a CCO backbone, and (ii) structural optimization in terms of porosity, and particle size distribution in the NiYSZ fuel electrode. The cell with the infiltrated oxygen electrode showed a worse initial performance, and a larger degradation rate as compared to SnA cell. The main part of the cell overpotential was related to the oxygen electrode. The degradation was, therefore, mainly due to degradation of this part of the cell. The microstructural analysis confirmed the results of electrochemical evaluation. The CCO backbone seems to be too coarse, and the LSC infiltrate not sufficiently well-dispersed to create the desired large active surface area.

The cell with optimized NiYSZ fuel electrode showed a superior initial performance and a small degradation rate, which can be related to a better fuel electrode microstructure. However, as the oxygen electrode (LSC-CGO) only contributed to a small extent to the overall cell resistance, the overpotential related to the fuel electrode was relatively large, which led to a predominant degradation of the fuel electrode. More specifically, Ni migration and loss of percolation led to an increase of both Rs and Rp under potentialistic conditions. Furthermore, larger leak was observed in this cell and cracks in the electrolyte have probably also contributed to the increase of Rs over time. However, these degradation phenomena were still not detrimental as compared to the overall degradation of the SnA Cell-A.

Appendix-A

Bode plots for the tested cells under fingerprint, before and after long-term testing were analyzed. This helped in the identification of individual electrode processes. Furthermore, the extent of leak current was visualized in this manner. The plotted values are the difference between the 50% steam and 20% steam conditions, with air and oxygen. To help understand the figures better, the following points can serve as a guide:

(i) Fuel-1: difference between 50% steam and 20% steam conditions, with oxygen on oxygen electrode
(ii) Fuel-2: difference between 50% steam and 20% steam conditions, with air on oxygen electrode
(iii) Fuel-avg: average of Fuel-1 and Fuel-2
(iv) Oxygen-1: difference between 20% steam conditions on fuel electrode, under oxygen and air
(v) Oxygen-2: difference between 50% steam conditions on fuel electrode, under oxygen and air
(vi) Oxygen-avg: average of Oxygen-1 and Oxygen-2

In theory, the Fuel average should lie on top of close to Fuel-1 and Fuel-2, and Oxygen average should lie close to Oxygen-1 and Oxygen-2. The distance between the average
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curve and the other two curves indicates the magnitude of leaks present in the cell test.

For Cell-A, in Figure 16 the magnitude of leak before the long-term test is low. After the long-term test, a significant deviation in the fuel electrode representation was found, which indicates that the leaks have increased, leading to a change in gas conversion and hence the interpretation of fuel electrode response is uncertain. The influence of the leaks on the oxygen electrode also increases after long-term testing, however, the individual and the average trends are similar. It clearly indicates the high degradation phenomenon experienced by the oxygen electrode. This confirms the observation from the DRT plots shown in Figure 7.

For Cell-B, leak present initially was higher than Cell-A as seen from Figure 17. However, the fuel and oxygen electrode responses can be easily distinguished. After the long-term test, there was a clear increase in the resistance for both oxygen and fuel electrode processes. Moreover, a shift in the summit frequency for the fuel electrode process was observed and this results in two different processes, one at a frequency of approximately 200 Hz relating to the increase in fuel electrode resistance [32], while the other at a frequency of 10 kHz remains unchanged in magnitude. The oxygen electrode response was observed at the same summit frequency while the magnitude increased, indicating towards a loss of active surface area [32]. The leak rate also increases since the difference between the two plots and the average has increased.

For the case of Cell-C, as seen from Figure 18, the magnitude of leak present before the long-term was significantly higher than the other two cells. However, fuel and oxygen electrode processes are distinguished easily. There was not a significant increase in leaks and the average response for fuel and oxygen remains equidistant from the plots. A significant shift in summit frequency was observed for the fuel electrode indicating to an increase in resistance. Oxygen electrode frequency remained similar and the magnitude of the resistance also remained unchanged.

Appendix B

The raw counts for the line scans during EDS analysis are displayed in Figure 18, “Inner” denotes the layer next to the electrolyte, right in the active fuel electrode. “Outer” denotes the layer in the active fuel electrode close to the support. “Support” denotes the line scan taken in the fuel electrode support. This was only performed for the Cell-C, and the reference cell, which is a sister cell to Cell-C and on which only initial characterization was done. The peak at 0.9 keV denotes the Ni content while for Y and Zr, the peaks are at 1.09 and 2.04 keV, respectively. Y and Zr peaks occur together. However, for the support the content differs and is clearly seen as a bend in the peak.

Fig. 16: Bode plots for Cell-A, (a) before, and (b) after long-term testing serving as a guide for electrode identification and the magnitude of leaks present.

Fig. 17: Bode plots for Cell-B, (a) before, and (b) after long-term testing serving as a guide for electrode identification and the magnitude of leaks present.

Fig. 18: Bode plots for Cell-C, (a) before, and (b) after long-term testing serving as a guide for electrode identification and the magnitude of leaks present.

Fig. 19: Raw counts from EDS analysis of (a) Reference cell/only initial fingerprint, and (b) Long-term tested cell (Cell-C).
From the comparison, the inner Ni content seems to deplete in relative terms to that of the reference cell. This shows the depletion of Ni in the layer next to the electrolyte, which is indicated as Ni migration. These counts are used to plot the graphs in Figure 15, by taking a ratio between Ni and (Ni+YSZ) counts.

Acknowledgements
The authors wish to thank Mr. H. Henriksen, Mrs. M. Davoudi, Dr. K. Thyden and Dr. S. Koch for technical help. The authors would also like to thank Dr. A. Hauch for her scientific insight, which helped enriching this work. The research leading to these results has received funding from the European Union’s Horizon 2020 framework program (H2020) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement no. 669892 (“Efficient Co-Electrolyser for Efficient Renewable Energy Storage-ECo”).

References
Durability of Solid Oxide Electrolysis stack under dynamic load cycling for syngas production
Durability of Solid Oxide Electrolysis stack under dynamic load cycling for syngas production

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Abstract

A 6-cell solid oxide electrolysis stack was tested under H₂O + CO₂ co-electrolysis condition. The cells used in the stack consist of a nickel-yttria stabilized zirconia (Ni-YSZ) fuel electrode, YSZ electrolyte and lanthanum strontium cobaltite-gadolinium doped ceria (LSC-GDC) composite oxygen electrode. The aim of this study was to investigate the stack durability when operated under dynamic load condition simulating a wind energy powered SOEC stack for syngas production. ASR degradation of the stack was observed to be less than 1%/1000 h during the 1000 hours operation. Electrochemical analysis revealed that the main degradation was associated to the fuel electrode. The overall stack voltage degradation rate at 0.4 A/cm² was 0.8%/1000 h.
Introduction

A shift in the energy production scenario, specifically for the case of Europe, is seen in the form of growing renewable energy generation. Moreover, in line with the EU 2050 goal, there is a need for lowering greenhouse gas (GHG) emissions. Most matured technologies for renewable energy production are solar and wind. However, they accompany a need for storage given the intermittent nature of power generation. Pumped hydro, compressed air and batteries are most well-known energy storage so far. In this context, electrolysis is a novel solution for highly efficient large-scale energy storage, in particular high temperature electrolysis using solid oxide electrolysis cells (SOECs). Power-to-Gas (PtG)/ Power-to-liquid (PtL) scenarios can be realized using SOECs, wherein CO₂ and steam can be combined to form syngas (CO+H₂). Furthermore, syngas can be converted downstream to produce hydrocarbons. In this regard, methane is of special interest owing to the availability of infrastructure for transport and storage in Europe.

One of the main issues associated with the application of SOECs is related to the durability of the cells and stacks. It is challenging to run SOECs for a shelf life of 5-10 years. Durability tests have been carried out under constant current in steam and co-electrolysis conditions. The cells have been tested at various operating parameters such as temperatures, gas compositions, current densities and voltages. For the State-of-the-art (SoA) with Ni-YSZ fuel electrode supported SOECs, the main degradation has been attributed to the fuel electrode such as Ni coarsening, Ni migration and loss of...
percolation\textsuperscript{15-19}. Degradation also finds its contribution in the oxygen electrode owing to the activity of the oxygen evolution reaction in the electrode\textsuperscript{20,21}, which is also dependent on the structure and composition of the oxygen electrode. Moreover, impurities in the gas stream effect the cell performance and durability\textsuperscript{13,22}.

Testing of SOECs are traditionally performed under galvanostatic conditions due to the ease of operation and data interpretation. A few tests have also been performed potentiostatically to understand the degradation of cells and the correlation between the testing modes and to approach realistic operating conditions at thermoneutral voltage\textsuperscript{23,24}. Considering the intermittent energy supply/storage, it is of importance to operate the stack under dynamic load conditions\textsuperscript{5} and evaluate the degradation during such operation mode. In this work, a 6-cell stack was tested under dynamic load operation simulated using the wind profile simulated for 24 hours, which is repeated over a period of 1000 hours.

Experimental

A stack with six cells produced by DTU Energy was assembled by SOLIDPower. The fuel electrode of the cells in stack was pre-reduced when received. Cells\textsuperscript{13} with 30 μm thick composite LSC-CGO oxygen electrode, a 6-7 μm thick CGO barrier layer, a 10 μm thick YSZ electrolyte, a 12–16 μm thick Ni-YSZ fuel electrode and a 300 μm thick Ni-YSZ support layer were used in the stack. The active area of one cell was 80 cm\textsuperscript{2}. The stack was tested in the setup described elsewhere\textsuperscript{25} and is displayed in Figure 1.
Initial characterization by electrochemical impedance spectroscopy (EIS) and iV curves (fingerprint) on each of the 6 cells of the stack was performed at 750 °C and 700 °C with the following fuel gas compositions supplied to the fuel electrode compartment:

1. 20% H₂O + 80 % H₂: 2.5 NL/min H₂O and 2.5 NL/min H₂
2. 50% H₂O + 50% H₂: 2.45 NL/min H₂O and 0.9 NL/min H₂
3. 80% H₂O + 20% H₂: 4.92 NL/min H₂O and 1.22 NL/min H₂
4. 90% H₂O + 10% H₂: 5.5 NL/min H₂O and 0.75 NL/min H₂
5. 45% CO₂ + 45% H₂O + 10% H₂: 3.4 NL/min CO₂ + 3.4 NL/min H₂O and 0.9 NL/min H₂
6. 25% CO₂ + 65% H₂O + 10% H₂: 1.9 NL/min CO₂ + 4.92 NL/min H₂O and 0.9 NL/min H₂

12 NL/min of oxygen or air was supplied to the oxygen electrode compartment.

EIS measurements were carried out using a Solartron 1252A frequency analyzer with a Kepco BOP 50-4M which was used to boost the 16 mA AC current from the Solartron to 1A AC and an external current transducer in series with the cell. The spectra were recorded from 96850 to 0.08 Hz with 12 points per decade and were corrected using the short circuit impedance response of the test setup. From the impedance spectra, the ohmic resistance (serial resistance, Rs) was taken as the value of the real part of the impedance at 25 KHz. The difference between the x-axis intercept and this value is very small. The polarization resistance (Rp) was then calculated as the difference in the real part of the impedance at 25 kHz and 0.1 Hz.

During the dynamic test, a constant flow of 65% H₂O + 25% CO₂ + 10%H₂ corresponding to 23% CO₂ + 2% CO + 8% H₂ + 67% H₂O in thermodynamic equilibrium composition was supplied to the
fuel electrode compartment and pure oxygen was supplied to the oxygen electrode compartment. The
gas composition to the fuel electrode was chosen aiming at the C-H ratio need for syngas production
for CH₄ synthesis. The simulated dynamic profile based on a daily wind profile is displayed in
Figure 2. This profile is repeated for 1000 hours of testing.

EIS measurements on the single cells during the dynamic durability tests were carried out at 0.4
A/cm² for the stack. EIS was also recorded at 0.25 A/cm² for the stack. Analysis of the impedance data
was performed using the software Ravdat.

Results and Discussion

Initial performance-iV and EIS under co-electrolysis

The 6-cell stack was characterized at 750 °C prior to the durability testing. In Figure 3, the i-V
(Figure 3(a)) and EIS (Figure 3(b)) are presented for the 6 cells characterized under co-electrolysis
conditions with O₂ supplied to the oxygen electrode compartment. The average cell open circuit
voltage (OCV) is 0.893 V, close to the theoretical OCV 0.897 V calculated by the Nernst equation
indicating a leak tight setup. From EIS, Cell-1 displays a higher Rs than the other cells which may be
related to a slightly bad electrical contact. For a better comparison, ASR obtained from the i-V curve
and EIS are listed in Table 1. The values from the i-V curves are taken in the linear regime as the slope
of the curve from 0 to 0.25 A/cm². Cell-1 has the highest ASR, which agrees with the EIS
measurements. All the other five cells have similar Rs varying within the range of 10%, but there is a
certain variation of the polarization resistances as well.

Table 1: ASR values during initial characterization with 65% H₂O + 25% CO₂ + 10% H₂ on fuel
electrode and O₂ on oxygen electrode

<table>
<thead>
<tr>
<th>Cell number</th>
<th>ASR from i-V curve (Ω cm²)</th>
<th>ASR from EIS (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.54</td>
<td>0.55</td>
</tr>
<tr>
<td>2</td>
<td>0.53</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>4</td>
<td>0.51</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>6</td>
<td>0.49</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**Durability test**

Following the initial fingerprint, the stack was tested under dynamic load conditions. The profile for
current density along with cell voltage evolution is shown in Figure 4(a). Figure 4(b) displays a zoom
of 50 hours for better viewing of voltage evolution of individual cells.

As can be seen from Figure 4(a) and (b), the maximum cell voltage was approximately 1.2 V at a
current density of 0.5 A/cm². Throughout the 1000 hours of durability testing, no significant change in
the stack voltage at the same current density was observed. The cell voltages exhibit an increase which
is in the order of 0.8%/1000 h. Cell-1 has a higher initial voltage, which also remains higher than all the
cells throughout the testing.

EIS spectra measured at 0.25A/cm² during durability testing are plotted in Figure 5. The profile was
repeated for 5 weeks of testing with constant flow and similar conversion arc, which is the low
frequency arc showing in the arc of the spectra on the right side.

It is worth to note that for Cycle-1, the measured fuel inlet temperature was 16 °C lower than during
the rest of the cycles; therefore, the change of EIS between cycle 1 and cycle 2 is most likely related to
the temperature difference. No change in conversion arc is seen for all the cycles illustrating constant
fuel utilization.

**Detailed resistance evaluation**

To analyze the degradation, ASR values were calculated as the sum of serial and polarization
resistance from EIS results.

To evaluate the performance and degradation in detail, ASR values are plotted in Figure 6(a).
Furthermore, contributions from Rs and Rp are further distinguished from EIS analysis and plotted in
Figure 6(b) and Figure 6(c) for each cell. No significant change of ASR is visible: the change of ASR is
below 1% per 1000 hours. It is worth to note that the initial increase in Rs and ASR in the first 200
hours coincides with the change of the stack temperature and is thus mainly related to this change
rather than a change of cell performance. No significant change of Rs and Rp is visible afterwards.
To further analyze the extent of degradation, firstly the average cell i-V is plotted under co-electrolysis conditions, before and after durability testing. This is displayed in Figure 7. A marginal change in performance can be seen. Change in OCV is also visible in the range of 5-10 mV.

In a further analysis, contributions from electrodes were separated from EIS recorded prior to and after durability testing. The EIS characterization before and after testing is shown in the form of Nyquist plots. In addition, Distribution of Relaxation Times (DRT) was used to separate the contributions from individual electrodes. By keeping the fuel electrode gas composition constant, the oxygen electrode gas was switched from air to oxygen. The response, in turn, is then related to the oxygen electrode. Similarly, by keeping the gas to the oxygen electrode constant and by varying the fuel electrode gas composition, the response of fuel electrode is indicated. The frequency response of the processes identified through this method can be found in Table 2.

Table 2: Identification of electrode response through DRT analysis performed in this work

<table>
<thead>
<tr>
<th>Process</th>
<th>Summit Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas conversion</td>
<td>1-3 Hz</td>
</tr>
<tr>
<td>Diffusion</td>
<td>10-20 Hz</td>
</tr>
<tr>
<td>Oxygen electrode reaction</td>
<td>100-500 Hz</td>
</tr>
<tr>
<td>Fuel electrode TPB reaction</td>
<td>800-1000 Hz</td>
</tr>
<tr>
<td>Fuel electrode charge transfer</td>
<td>10-20 KHz</td>
</tr>
</tbody>
</table>
Further, in Figure 8 the response of the individual electrodes is clearly displayed as measured at OCV. In figure 8(a), steam content is changed and the response of fuel electrode triple phase boundary reaction as well as charge transfer is visible at high frequencies i.e., at approximately 800-1000 Hz and 12-15 kHz. For the oxygen electrode response, in Figure 8(b) the arrow indicates the frequency of approximately 200-500 Hz.

Furthermore, EIS were evaluated during operation and for the individual cells. Due to temperature fluctuations around 200 hours, data treatment is performed after 250 hours for DRT analysis to have consistency in analysis. Figure 9 displays part of the DRT spectra emphasizing the fuel and oxygen electrode contribution at 0.4 A/cm² is displayed over a period of 1000 hours of testing. The EIS spectra are plotted for every 200 hours approximately. It should be noted that Figure 8 displays the OCV conditions while Figure 9 is under current which implies a shift in frequency response. All the cells exhibit degradation particularly in the frequency of 500 Hz to 3 kHz. Deducing from Figure 9(a), the fuel electrode of cell-1 seems to degrade around 1-3 kHz, which is also the case for the cells shown in Figure 9(c), and (f). However, for the cells shown in Figure 9(b), (c), and (d), both the fuel and oxygen electrode degrade which can be seen in the form of an additional arc at approximately 500-800 Hz.

In order to understand the contribution from electrodes to the total ASR, the overpotential was calculated according to the following equation:

\[ \eta_p = V - OCV - IR_s \]

where, \( \eta_p \) is the overpotential, \( V \) is the measured voltage under current, \( OCV \) is the measured OCV, \( I \) is the operating current density and \( R_s \) is the serial resistance.
The overpotential for all the cells of the stack at a current density of 0.4 A/cm$^2$ was calculated at the beginning and the end of the durability test and is displayed in Table 3. Beginning of the test refers to 257 h, similar to Figure 9 since only responses at similar temperature can be directly compared.

Table 3: Overpotential of the cell (excluding serial resistance)

<table>
<thead>
<tr>
<th>Cell number</th>
<th>Overpotential (mV) (Beginning of the durability test, $t=257$ h)</th>
<th>Overpotential (mV) (End of the durability test, $t=1000$ h)</th>
<th>Change in overpotential (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>82.2</td>
<td>86.3</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>97</td>
<td>100.9</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>104.6</td>
<td>108.4</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>100.4</td>
<td>109.5</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>111.7</td>
<td>113.4</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>117.6</td>
<td>120</td>
<td>2</td>
</tr>
</tbody>
</table>

Previous studies have reported the loss of active Ni network due to Ni migration as a major contribution to the degradation of such cells$^{15}$. By running the stack under dynamic load, the cells in the stack are exposed to various current densities. However, the maximum current density is limited to 0.5 A/cm$^2$. This means that the overpotential experienced by the cells is in the threshold of reversible degradation, where no major Ni particle rearrangements or losses should occur$^{15}$. 
The stack was not exposed to high current density (high overpotential) for a long time which led to less degradation, thereby indicating an optimal operating window for long term conversion of excess renewable energy. This is plotted in the form of power density and hydrogen production during dynamic cycling in Figure 10. The power density follows the current density such that no significant change is observed thereby indicating nominal performance during 1000 hours of operation. The accumulated syngas production throughout the 1000 hours calculated based on the current was approximately 3074 moles (258 m³ @ 25°C).

Conclusion

This work serves as a proof of concept for dynamic operation of SOEC in co-electrolysis mode for application as storage of electricity from renewable sources, i.e. a viable Power-to-Liquid/Power-to-Gas scenario. Operating the SOEC stack at a maximum current density of 0.5 A/cm² revealed insignificant degradation under co-electrolysis condition. ASR degradation of less than 1%/1000 h was observed, and constant gas conversion impedance at 0.4 A/cm² for all the cells of the stack indicated even distribution of the gas flows. Change in fuel electrode response around 1 kHz along with oxygen electrode response around 500 Hz indicated an only minor degradation effect. The formed synthesis gas can be further converted into for example methane through well-known catalytic processes and stored and distributed in the existing infrastructure as synthetic natural gas.
Acknowledgements

The author wishes to thank Mr. H. Henriksen, Mr. Ole Hansen, Dr. J. Høgh, Dr. S. Pitscheider, Dr. N. Seselj and Dr. A. Ploner for their technical help with measurement and testing. The research leading to these results has received funding from the European Union’s Horizon 2020 framework program (H2020) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement no. 699892 (“Efficient Co-Electrolyser for Efficient Renewable Energy Storage-ECo”).

References


23. Rao, M., Sun, X. & Hagen, A. A Comparative Study of Durability of Solid Oxide Electrolysis


**Figures and Captions**


Figure 1: Stack test setup with furnace and stack mounting images

Figure 2: Simulated daily wind profile for the stack test
Figure 3(a): i-V curves for the 6 cells in the stack tested with 65% H₂O + 25% CO₂ + 10% H₂ on fuel electrode and O₂ on oxygen electrode at 750 °C
Figure 3(b): Nyquist plot for each cell in the 6-cell stack tested with 65% H₂O + 25% CO₂ + 10%H₂ on the fuel electrode and O₂ on the oxygen electrode under 1A DC at 750 °C.
Figure 4(a): Voltage evolution as a function of time during durability testing with 65% H₂O + 25% CO₂ + 10% H₂ on the fuel electrode and O₂ on the oxygen electrode (i in the legend refers to the current density profile followed during testing) at 750 °C.

Figure 4(b): Voltage evolution shown for a selected period of 50 hours of operation during durability testing with dynamic load (black curve, right axis).
Figure 5: Plots displaying evolution of EIS during durability testing, recorded at 0.25 A/cm² for cells in the stack.
Figure 6: ASR, $R_e$, $R_p$ evolution during durability from EIS at 0.4 A/cm$^2$

Figure 7: i-V curves before and after durability test with 5% H$_2$O + 25% CO$_2$ + 10% H$_2$ on the fuel electrode and O$_2$ on the oxygen electrode at 750 °C
Figure 8: DRT plots showing frequency response (a) fuel electrode, and (b) oxygen electrode at OCV of Cell-3 of the stack (Arrows indicate the frequency ranges for the responses from both electrodes)
Figure 9: DRT plots zooming in on degradation of fuel and oxygen electrode for cells in the stack
Figure 10: H₂ production and power density during durability testing