

The Utilization of Seawater and Wastewater in Solid Oxide Electrolysis Cells

Die Verwendung von Meerwasser und Abwasser in Hochtemperatur Festoxid Elektrolysezellen

Von der Fakultät für Mathematik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades eines Doktors der Ingenieurwissenschaften genehmigte Dissertation

vorgelegt von

Jan Uecker, M.Sc.

aus

Wesel

Berichter: Univ.-Prof. Dr. rer. nat. Rüdiger-Albert Eichel

Univ.-Prof. Dr. rer. nat. Simon Ulrich

Univ.-Prof. (em.) Dr.-Ing. Lorenz Singheiser

Tag der mündlichen Prüfung: 06.03.2026

Diese Dissertation ist auf den Internetseiten der Universitätsbibliothek verfügbar.

Eidesstattliche Erklärung

Ich, Jan Uecker, erkläre hiermit, dass diese Dissertation und die darin dargelegten Inhalte meine eigenen sind und selbstständig, als Ergebnis meiner eigenen originären Forschung, generiert wurden.

Hiermit erkläre ich an Eides statt:

1. Diese Arbeit wurde vollständig oder größtenteils in der Phase als Doktorand dieser Fakultät und Universität angefertigt;
2. Sofern irgendein Bestandteil dieser Dissertation zuvor für einen akademischen Abschluss oder eine andere Qualifikation an dieser oder einer anderen Institution verwendet wurde, wurde dies klar angezeigt;
3. Wann immer andere eigene Veröffentlichungen oder Veröffentlichungen Dritter herangezogen wurden, wurden diese klar benannt;
4. Wenn aus anderen eigenen Veröffentlichungen oder Veröffentlichungen Dritter zitiert wurde, wurde stets die Quelle hierfür angegeben. Diese Dissertation ist vollständig meine eigene Arbeit, mit der Ausnahme solcher Zitate;
5. Alle wesentlichen Quellen von Unterstützung wurden benannt;
6. Wann immer ein Teil dieser Dissertation auf der Zusammenarbeit mit anderen basiert, wurde von mir klar gekennzeichnet, was von anderen und was von mir selbst erarbeitet wurde;
7. Ein Teil oder Teile dieser Arbeit wurden zuvor veröffentlicht. Eine Auflistung findet sich auf Seite 138.

Ort, Datum, Unterschrift

Danksagung

Die vorliegende Dissertation ist in der Zeit von Mai 2022 bis Mai 2025 entstanden. Es waren drei spannende, lustige und lehrreiche, aber auch anstrengende Jahre. Durch Höhen und Tiefen wurde ich begleitet durch Kollegen, Freunde und Familie, denen ich gerne meinen Dank entgegenbringen möchte.

Ich möchte mich bei Prof. Rüdiger-A. Eichel für die Möglichkeit bedanken, meine Promotion am IEK-9 bzw. IET-1 im Forschungszentrum Jülich durchführen zu dürfen, und für die Unterstützung und Impulse, die es von seiner Seite in Gesprächen immer gegeben hat.

Des Weiteren möchte ich mich bei Prof. Ulrich Simon und Prof. Lorenz Singheiser für die Bereitschaft bedanken, Gutachter dieser Arbeit zu sein. In dem Zuge möchte ich meinen Dank auch an Prof. Granwehr aussprechen, der immer ein offenes Ohr für wissenschaftliche Diskussionen hatte.

Einen besonderen Dank möchte ich an Dr. Ico Vinke und Dr. Bert de Haart aussprechen, die mich wissenschaftlich immer unterstützt haben.

Ein ebenso großer Dank gilt meinen Kolleginnen und Kollegen, Tanja Brambach, Claudia Tropartz, Britta Bär und Mathias Westermann für die Unterstützung im Labor und die schönen Gespräche.

Bei Dr. Lucy Nohl, Dr. Markus Nohl, Dr. Stephanie Wolf, Dr. Vaibhav Vibhu, Leon Schley und Severin Foit bedanke ich mich für den fachlichen Austausch und die Unterstützung in allen Belangen, wodurch aus Fremden Freunde wurden.

Zudem bedanke ich mich bei Rishabh Kumar und Saranya Thankappakurup, die erst später zur Gruppe dazugestoßen sind und mit ihrer positiven Einstellung eine Bereicherung darstellen. In diesem Zusammenhang möchte ich mich bei Dr. Till Frömling bedanken, der zwar erst in den letzten fünf Monaten meiner Doktorarbeit als Abteilungsleiter zur Gruppe dazugestoßen ist, mich aber direkt in wissenschaftlichen und persönlichen Fragen unterstützt hat.

Ich möchte mich auch bei Niklas Eyckeler, Luca Inkmann, Chenlu Li und Bintou Issa Dembele bedanken, die ihre Forschungs-, Bachelor- oder Masterarbeiten bei mir bzw. bei uns am Institut absolviert haben. Für euer Engagement und die tolle Zusammenarbeit danke ich euch. Für die moralische und wissenschaftliche Unterstützung möchte ich mich zusätzlich bei Christian Mänken, Jean-Pierre Puc, Laurin Hensen, Sebastian Speer, Ifeanyichukwu Unachukwu, Pritam Chakraborty, Malte Wehner und Stefan Blaschke bedanken. Es war eine großartige Zeit mit euch!

Nicht zuletzt geht mein Dank an die Verwaltung des Instituts: Birgit Derksen, Michaela Fittkau, Sandra Hoffmann, Madita Kaul, Seline Tosun und Katharina Nickel. Denn für gute Wissenschaft braucht es nicht nur gute Wissenschaftler! Ohne euch würde das Institut nicht funktionieren.

Meiner Familie und meinen Freunden danke ich dafür, dass sie immer ein offenes Ohr für mich hatten und sich mit mir gefreut oder wenn nötig motiviert und aufgebaut haben.

Mein größter Dank geht an meine Frau, an meine Eltern und meine gesamte Familie, ohne die ich nicht hier wäre. Ihr habt mich immer unterstützt und gefördert und dafür danke ich euch von ganzem Herzen!

Kurzfassung

Die Verwendung von Meer- und Abwasser stellt eine Möglichkeit dar, den Druck auf Frischwasserressourcen für die Wasserstoffherstellung zu verringern. Die Hochtemperaturelektrolyse zeichnet sich durch erhöhte Effizienzen bei den Operationstemperaturen von 700 bis 900 °C aus.

In dieser Arbeit werden kommerzielle Festoxidzellen auf Ihre Komptabilität mit salzhaltigem Wasser untersucht. Dabei werden die Leistung und die Stabilität betrachtet. Zudem wird eine Lösung auf Systemebene für die Verwendung in Hochtemperaturelektrolyseanlagen diskutiert. Aus den Vergleichsmessungen mit ultrapurem Wasser konnte gezeigt werden, dass das Degradationsverhalten der Zellen im Betrieb stark von den Batches der Zellen abhängt, wobei Vergiftungen mit Silizium in den Ausgangsmaterialien kritisch zu sehen sind.

Die Verwendung von Meerwasser zeigte keinen Einfluss auf die initiale Leistung der Zellen. Allerdings wurde eine erhöhte Degradationsrate über 1000 Stunden Betriebszeit aufgrund von Verlusten in der Ni-YSZ Brenngaselektrode durch Siliziumvergiftungen beobachtet. Der Transport von Salz und dessen Ablagerung auf der Zelle wurde bestätigt. Interessanterweise wurden herkömmliche Degradationsmechanismen durch die Verwendung von Meerwasser unterdrückt, was auf eine Stabilisierung der Mikrostruktur in der Ni-YSZ Brenngaselektrode zurückgeführt wurde.

In einem Test mit erhöhter Natriumchloridkonzentration wurde ebenfalls kein Einfluss auf die anfängliche Leistung beobachtet. Allerdings wurde eine erhöhte Degradationsrate in einem Langzeitversuch über 1000 Stunden beobachtet, welche auf Verluste in der Ni-YSZ Brenngaselektrode zurückzuführen ist. Es wurde eine Natriumcarbonatspezies auf der Elektrode mithilfe von SEM-EDX gefunden. Auf Basis der Erkenntnisse wurde ein Mechanismus vorgeschlagen, in dem gasförmige Salzsäure gebildet wird, welche für die erhöhte Degradation verantwortlich ist.

Im letzten Schritt wurde eine technische und ökonomische Analyse durchgeführt, bei der die Verwendung eines Fallfilmverdampfers gekoppelt mit einem Hochtemperaturelektrolysesystems für die Meerwasserverwendung evaluiert wurde. Dies wurde mit einem System basierend auf einer Umkehrosmose und einem konventionellen Verdampfer verglichen. Es wurde gezeigt, dass ein ökonomischer Vorteil durch die simultane Verdampfung und Aufreinigung von Meerwasser wahrscheinlich ist. Allerdings besteht ein erhöhtes technische Risiko.

Insgesamt konnte gezeigt werden, dass Meerwasser und Abwassernutzung in der Hochtemperaturelektrolyse zukünftiges Potential bieten, allerdings kann der Transport von Salzen oder anderen Verunreinigen problematisch für das System sein. In dieser Arbeit wurde speziell herausgestellt, dass Silizium (in Meerwasser) oder Natriumchlorid problematisch für die Zellstabilität sind und vorher herausgefiltert werden müssen.

Abstract

The utilization of seawater and wastewater is one way of reducing the pressure on freshwater sources for the production of hydrogen. High temperature electrolysis is an interesting approach due to the increased efficiencies at operating temperatures of 700 – 900 °C.

In this work, commercially available solid oxide cells were analyzed for operation with saline containing water. The electrochemical performance and long term stability were evaluated, and a novel system level concept for seawater utilization in high temperature electrodes was assessed.

For pure water operation, acting as reference, degradation behavior strongly depended on cell production conditions, with silicon contamination from starting materials identified as a critical factor. Thus, long term stability testing with saline water utilization should be only compared against benchmark pure water operation from the same cell production batch.

The use of seawater showed no influence on the initial performance and activation energies of the cells. However, an increased degradation rate over 1000 hours of operation was observed due to polarization losses in the Ni-YSZ fuel electrode. This was correlated to silica poisoning detected by post test characterization. Additionally, the transport of salt was confirmed by deposits found on the surface of the Ni-YSZ fuel electrode. Interestingly, conventional degradation mechanisms were suppressed by seawater usage, which was attributed to a stabilization of the microstructure in the Ni-YSZ fuel gas electrode.

Electrochemical measurements with saturated sodium chloride solution revealed no negative effect on the initial performance and activation energies. However, an increased degradation rate was observed, which can be attributed to polarization losses in the Ni-YSZ fuel electrode. A sodium carbonate species was detected by post test characterization on the fuel electrode surface. The findings suggested a mechanism in which gaseous hydrochloric acid is formed, contributing to accelerated Ni agglomeration in the electrode and leading to increased degradation.

In the final step, the use of a falling film evaporator coupled with a high temperature electrolysis system for seawater utilization was evaluated through technical and economic analysis. This was compared with a system based on a reverse seawater osmosis unit and a conventional evaporator. It was shown that the simultaneous evaporation and purification of seawater is likely to provide an economic advantage. However, there is an increased technical risk.

It was shown that seawater and wastewater utilization in high temperature electrolysis offer future potential, but the transport of salt or other impurities can be problematic for the system. In this work, it was specifically emphasized that silicon, e.g. in seawater or sodium chloride, is problematic for cell stability and must be filtered out beforehand.

List of Abbreviations and Parameters

AC	Alternating Current
BOP	Balance of Plant
BSE	Back Scattered Electron
C	Capacitor
CAPEX	Capital Expenditure
CNLS	Complex Nonlinear Least Square Fitting
CPE	Constant Phase Element
DRT	Distribution of Relaxation Time
ECM	Equivalent Circuit Model
EDX	Energy-dispersive X-Ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FFE	Falling Film Evaporator
GDC	Gadolinium-Doped Ceria
GI-XRD	Glancing Incidence X-Ray Diffraction
I	Inductor
ICP-OES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LCOH	Levelized Cost of Hydrogen
LSC	$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$
LSCF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$
MIEC	Mixed Ionic and Electronic Conductors
MFC	Mass Flow Controller
OCV	Open Circuit Voltage
OPEX	Operational Expenditure
PEM	Proton Exchange Membrane
R	Resistor
RO	Reverse Osmosis
RSOC	Reversible Solid Oxide Cell
Si	Silicon
SDR	Degradation Rate (%)
SOC	Solid Oxide Cell
SOEC	Solid Oxide Electrolysis Cell
SOFC	Solid Oxide Fuel Cell
SWRO	Seawater Reverse Osmosis
SEM	Scanning Electron Microscopy
TPB	Triple Phase Boundary

XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
YSZ	Yttrium Stabilized Zirconia
3YSZ	3 mol% Yttrium Stabilized Zirconia
8YSZ	8 mol% Yttrium Stabilized Zirconia
ASR	Area Specific Resistance ($\Omega \cdot \text{cm}^2$)
D^{eff}	Effective Diffusion Coefficient
E	Potential (V)
E_0	Reversible Cell Voltage (V)
E_a	Activation Energy ($\text{J} \cdot \text{mol}^{-1}$)
E_{cell}	Cell Potential (V)
F	Faraday Constant ($\text{As} \cdot \text{mol}^{-1}$)
G_f	Gibbs Free Energy of Formation (J)
H_f	Formation Enthalpy (J)
I	Current (A)
c	Concentration (mol)
i	Current Density ($\text{A} \cdot \text{cm}^{-2}$)
i_0	Exchange Current Density ($\text{A} \cdot \text{cm}^{-2}$)
i_L	Limiting Current Density ($\text{A} \cdot \text{cm}^{-2}$)
n	Number of Exchanged Electrons ()
m	Mass (g)
$R_{\text{diff.}}$	Gas diffusion and conversion resistance (Ω)
R_g	Gas Constant ($\text{As} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
R_p	Polarization Resistance (Ω)
R_{total}	Overall Resistance (Ω)
R_{Ω}	Ohmic Resistance (Ω)
R_o	Exponential Facotr
S_f	Formation Entropy ($\text{J} \cdot \text{K}^{-1}$)
T	Temperature (K)
t	Time (s)
Z	Impedance (Ω)
α	Transfer coefficient ()
λ	Regularization Factor
η	Overpotential (V)
ρ	Partial Pressure (bar)
σ_0	Conductance (S)

τ	Time Constant (s)
δ	Layer thickness (cm)
ϕ	Phase Shift (rad)
ω	Radial Frequency ($\text{rad} \cdot \text{s}^{-1}$)

Contents

1 Motivation	1
2 Solid Oxide Electrolysis Cells	3
2.1 Working Principle	3
2.2 Thermodynamics	5
2.3 Degradation Behavior	6
3 Electrochemical Methods	9
3.1 Current Voltage Characteristics	9
3.1.1 Open Circuit Voltage	9
3.1.2 Polarization Losses	9
3.2 Electrochemical Impedance Spectroscopy.....	11
3.2.1 Equivalent Circuit Model.....	13
3.2.2 Distribution of Relaxation Times	15
3.2.3 Application for Solid Oxide Cells.....	16
4 State of the Art.....	19
5 Experimental.....	25
5.1 Measurement Setup.....	25
5.2 Electrolysis Cell	26
5.3 Electrochemical Characterization	27
5.4 Post characterization	28
5.5. Techno-Economic Analysis	29
5.5.1 Implementation in Aspen Plus	29
5.5.2 Modeling of the System Components	31
5.5.5 Optimization of the Heat Consumption	31
5.5.6 Techno Economic Assessment.....	32
6 Results and Discussion	35
6.1 Stability in Pure Water Operation	35
6.1.1 Long Term Stability Measurement	36
6.1.2 Post Test Characterization	46

6.2 Direct Utilization of Seawater	51
6.2.1 Electrochemical Initial Performance.....	52
6.2.2 Stability Evaluation	59
6.3 Direct Saturated Sodium Chloride Solution Utilization	81
6.3.1 Electrochemical Initial Performance.....	82
6.3.2 Long Term Stability Test.....	84
6.4 Techno Economic Evaluation of Seawater Electrolysis	100
6.4.1 Process Approaches	101
6.4.2 Heat Demand and Integration.....	101
6.4.3 Electricity Demand.....	104
6.4.4 Techno Economic Evaluation	105
7 Summary and Outlook	109
8 Literature.....	113
9 Appendix.....	125
9.1 Tables.....	125
9.2 Figures.....	131
9.3 Publications, Patents and Conference Contributions.....	138
9.3.1 Publications	138
9.3.2 Patents	140
9.3.3 Conference Oral and Poster Contributions	140
9.4 Figure Directory	141
9.5 Table Directory	145

1 Motivation

The rising concentration of global greenhouse gases due to human activities sparks the need for a transition in the energy sector from fossil fuels to sustainable energy sources to mitigate global warming. Sustainable power sources include solar photovoltaic, wind and hydropower with solar radiation offering the greatest potential ^[1]. Efficient conversion and storage technologies are essential for managing seasonal fluctuations and enabling long distance energy transport. Here, electrolysis technologies can convert renewably generated electrical energy into chemical energy carriers for storage and transportation. The electrochemical splitting of water produces hydrogen, which is promising due to its high gravimetric energy density ^[1].

State-of-the-art electrolysis technologies for hydrogen production rely almost exclusively on freshwater of high purity ^[2]. The freshwater supply is expected to become more erratic and uncertain, and freshwater demand will increase in the next few years ^[3-4]. For instance, projections indicate that the number of urban residents facing water scarcity will grow from 933 million in 2016 (approximately one third of the global urban population) to 2.4 billion by 2050 ^[5]. This issue is particularly acute in regions such as Africa, South America, and Australia, which possess high solar irradiation potential and are thus promising candidates for hydrogen production. However, water scarcity is expected to rise in these regions and could be exacerbated by the deployment of electrolyzer systems ^[4, 6-7].

One strategy to relieve pressure on freshwater resources is to utilize alternative water sources, such as seawater and industrial wastewater. Recent studies have investigated the feasibility of seawater in various electrolysis systems with different technological approaches ^[8-11]. The utilization of industry wastewater with higher salt content is another solution that has not been discussed in the literature until now. A particularly promising approach is the high temperature solid oxide electrolysis cell (SOEC), which uses steam instead of liquid water due to operating temperatures of around 800 °C. Thus, competitive and parasitic reactions like the chlorine evolution reaction are not expected to occur, which is a significant problem in room temperature technologies such as alkaline electrolysis ^[12-13].

While a few studies have evaluated the direct use of seawater in SOECs, a comprehensive scientific, technical, and economic assessment is still lacking ^[9, 14-15]. Moreover, the long term stability of SOECs with higher concentrated saline waters is missing in literature.

Therefore, this thesis focuses on the evaluation of saline water utilization in SOEC systems. The goal is to understand degradation mechanisms, identify technical challenges, and assess economic feasibility. This work aims to close existing gaps in the literature by combining detailed electrochemical investigations with system level analysis, providing a holistic perspective on the potential of saltwater fed high temperature electrolysis.

2 Solid Oxide Electrolysis Cells

2.1 Working Principle

Solid oxide cells (SOCs) are high temperature electrochemical devices capable of both energy conversion and storage. They are operated at elevated temperatures between 650 and 900 °C and are designed to function in both fuel cell (SOFC) and in electrolysis (SOEC) modes using the same cell design as a key feature ^[16]. The ability to switch reversibly between these modes gives rise to the term reversible solid oxide cell (RSOC). A key advantage of SOC is their operational flexibility with various feedstocks such as carbon based fuels, hydrogen, and ammonia in SOFC mode, and steam or carbon dioxide in SOEC mode. A schematic overview of such a system is shown in Figure 1.

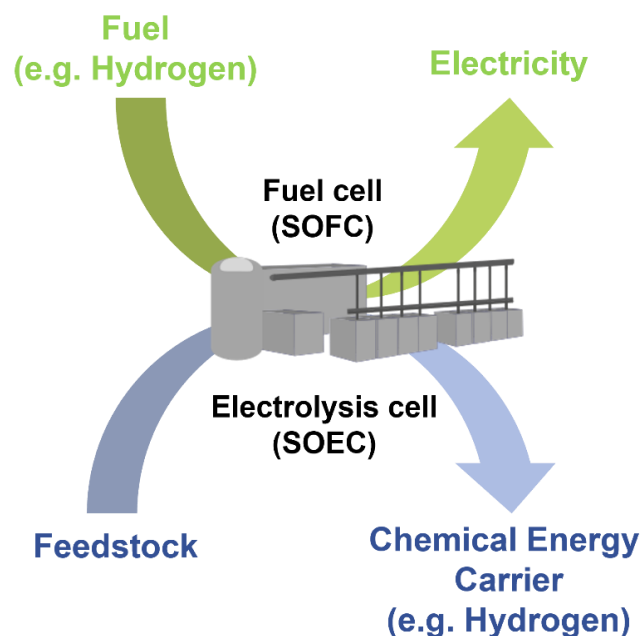


Figure 1 Representation of a reversible and flexible operable SOC system.

Recent research has increasingly focused on SOECs due to their potential for efficient hydrogen production and energy storage. Structurally, SOC is a ceramic based device consisting of three essential components: an oxide ion conductive electrolyte sandwiched by cermet (ceramic metal composite), metal, or ceramic electrodes. The electrolyte requirements are gas tightness, high ionic conductivity, and low electronic conductivity. The electrodes are the active layers where the electrochemical reaction occurs and must offer sufficient electronic and ionic conductivity to support high electrochemical performances.

It is important to note that a steam generator is placed upstream of the SOEC system for water electrolysis; thus, the term steam electrolysis is often used ^[16].

In the case of steam electrolysis, power is supplied to split steam into hydrogen and oxygen. At the cathode, steam is reduced under the release of hydrogen and the formation of O^{2-} ions (Equation 2.1), which act as charge carriers through the solid electrolyte. These O^{2-} ions are oxidized at the anode, releasing molecular oxygen and electrons. The latter are introduced into the outer electrical circuit (Equation 2.2). The overall reaction is given in Equation 2.3. A schematic representation of a SOC operated in SOEC or SOFC mode in a steam and hydrogen atmosphere is provided in Figure 2. To ensure sufficient O^{2-} conductivity in the electrolyte and the electrodes high operating temperatures between 650 to 900 °C are required.



It is worth noting that SOECs can be operated in co-electrolysis, where both steam and CO_2 are simultaneously split ^[17]. However, this thesis focuses exclusively on steam electrolysis. In recent years, the electrode denotation of the fuel electrode for the cathode and the air electrode for the anode in electrolysis operation is preferred to avoid confusion caused by the possible switching between electrolysis and fuel cell operation and the consecutive switching of the denotation's anode and cathode. Thus, the terms fuel and air electrode are adopted consistently throughout the manuscript.

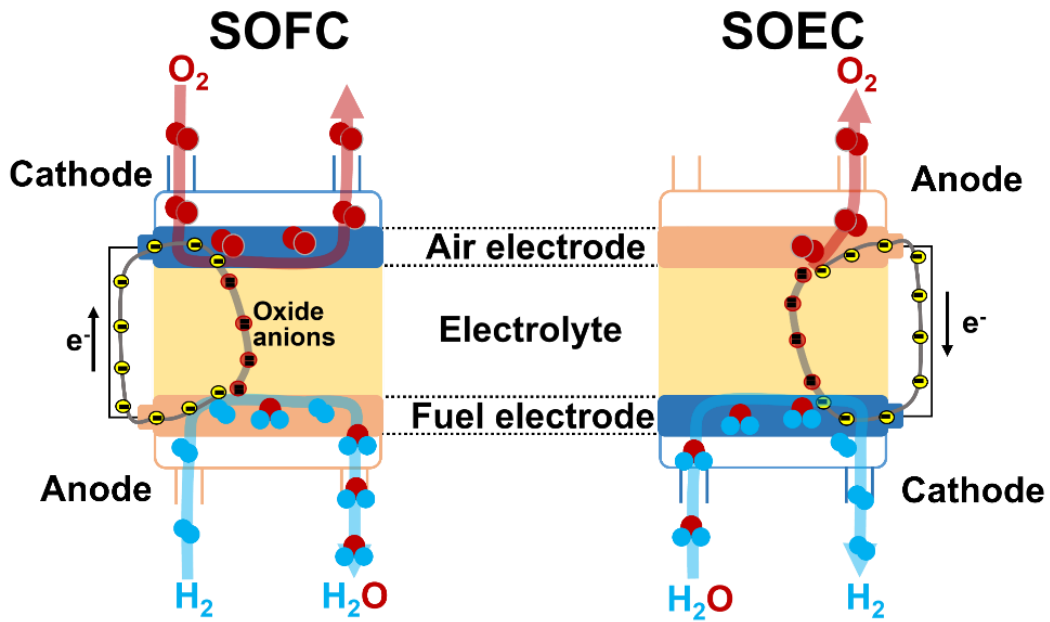


Figure 2 Schematic representation of the working principle of a SOC operated in SOFC and SOEC mode in a H_2/H_2O system.

2.2 Thermodynamics

Among available electrolysis technologies, high temperature electrolysis systems are thermodynamically the most efficient. The thermodynamic minimum total energy demand for water splitting is given by the formation enthalpy ΔH_f . ΔH_f consists of an electric contribution, which is the Gibbs free energy of formation ΔG_f and a thermal contribution, including the entropy of formation ΔS_f and the temperature T as expressed in Equation 2.4. The high temperature reduction of H_2O is an endothermic reaction and ΔS_f is positive.

$$\Delta H_f = \Delta G_f + T\Delta S_f \quad (2.4)$$

The minimum (reversible) cell voltage E_0 is calculated from ΔG_f as shown in Equation 2.5 in the case of equilibrium gas conditions with n as the number of exchanged electrons and F as the Faraday constant.

$$\Delta G_f = -nFE_0 \quad (2.5)$$

Figure 3 illustrates the thermodynamic energy demands and the corresponding cell voltages for steam electrolysis across a temperature range from 0 to 1000 °C at atmospheric pressure. The total energy demand of formation stays relatively constant over a temperature range from 100 to 1200 °C. At 100 °C, the evaporation heat of water is responsible for the drop in total energy and thermal energy demand. The thermal contribution increases with temperature, whereas the electric contribution decreases. Thus, an increasing amount of the total energy demand can be supplied by heat accompanied by an increase in operating temperature. Concerning this, the required minimum cell voltage is decreasing. Additionally, elevated temperatures enhance reaction kinetics, which further improves overall efficiency [18-19].

A comparison of the typical ranges of cell voltage versus the current density for SOECs, alkaline electrolysis cells and proton exchange membrane (PEM) electrolysis cells in water electrolysis operation is shown in Figure 4. Here, the effects of thermodynamics correspond to significantly improved electrical efficiency of SOECs compared to other technologies. E_{th} in the plot refers to the thermoneutral voltage where the SOEC operation supplies exactly the power necessary to meet the required heat for the endothermic water splitting reaction. From the figure, SOECs are the go to option for the hydrogen economy due to their higher efficiency compared to other low temperature systems. However, SOEC systems need high startup and shut down times and the scale up is difficult due to the balance of plant (BOP) components [19]. Furthermore, the long term stability in SOECs is still an issue, which will be discussed further in the next section [21].

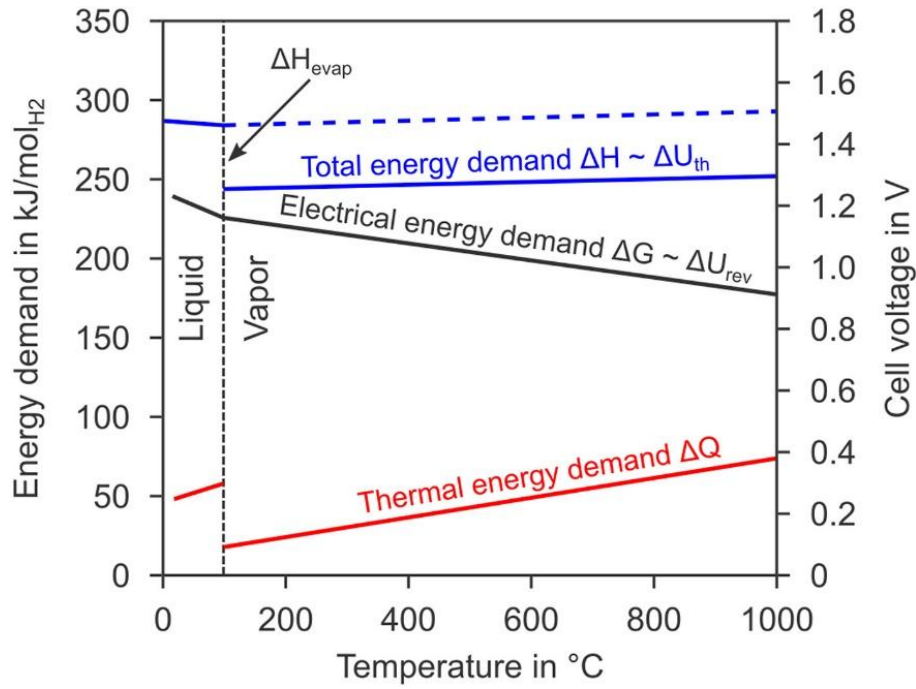


Figure 3 Illustration of the total energy demand, heat demand and electricity demand based on thermodynamics of water electrolysis with typical ranges of cell voltages taken from ^[20].

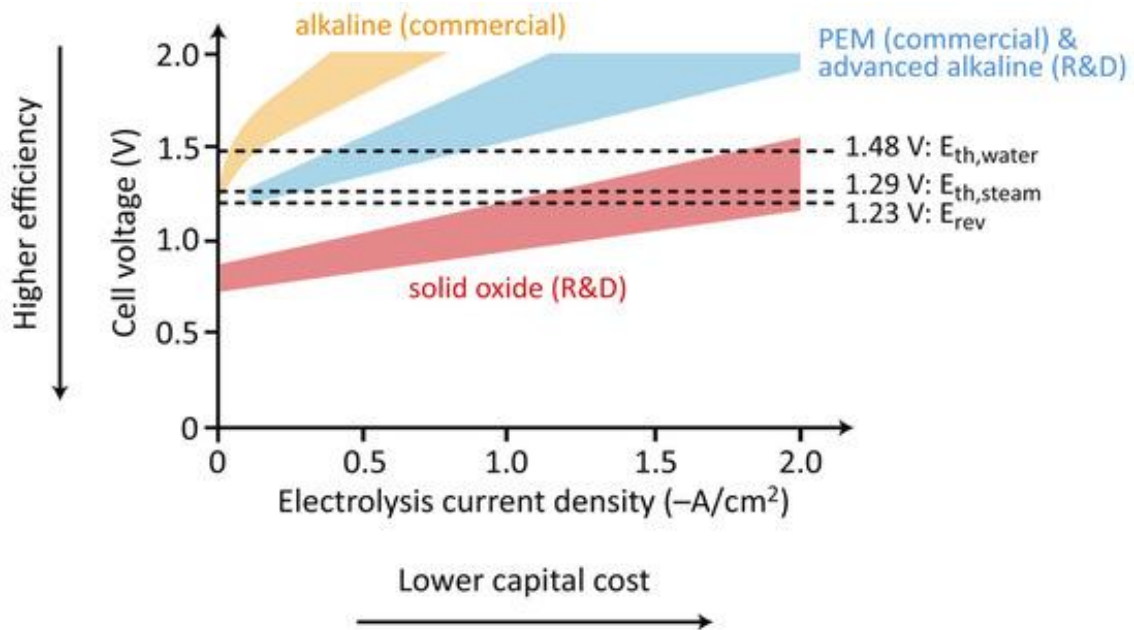


Figure 4 Typical voltage ranges as a function of current density for water electrolysis of low temperature and high temperature cells taken from ^[22].

2.3 Degradation Behavior

On a system level, all components of a SOEC system need the lowest possible degradation rates to be commercially feasible. Here, rates between 0.5 and 0.75 %/kh⁻¹ need to be reached, corresponding to around 20 % performance loss over 5 years ^[21]. Reported degradation rates in the literature vary widely depending on operating conditions, ranging from

0.5 % to over 5 %/kh ^[23-26]. Notably, lower degradation rates are mainly recorded at low current densities of around $-0.5 \text{ A}\cdot\text{cm}^{-2}$, whereas a practical operation at thermoneutral operation (1.29 V) corresponds to much higher current densities of $-1.5 \text{ A}\cdot\text{cm}^{-2}$ ^[19].

Degradation is predominantly attributed to the state-of-the-art Ni based fuel electrodes, especially Ni-YSZ and Ni-GDC, which are favored for their high catalytic activity and affordability ^[27-28]. Between both, Ni-YSZ is still the most studied material ^[28]. In Ni-YSZ fuel electrodes, the water splitting happens at the triple phase boundaries (TPB) between the electrical conducting phase (Ni), the ionic conducting phase (YSZ) and the gas phase ($\text{H}_2\text{O}/\text{H}_2$). Common degradation mechanisms include Ni migration, agglomeration, and depletion, all of which reduce electrochemical performance ^[29-31].

In addition, impurity transport can damage the electrode microstructure or block active sites ^[32-34]. Figure 5 visually summarizes key degradation mechanisms leading to a reduction of the active TPB length. For instance, the depletion of Ni is leading to inactive zones near the electrolyte. Other degradation mechanisms not shown here include the delamination of layers or the fracturing or cracking of the electrolyte ^[21, 35].

Delamination issues are often connected to the air electrode as the delamination is attributed to the evolution of oxygen where the oxygen penetrates pores of the electrode/barrier layer/electrolyte interfaces and builds up an oxygen gradient under anodic polarization ^[36-37]. Increases in ohmic resistance during SOEC operation are frequently attributed to this phenomenon ^[30-31].

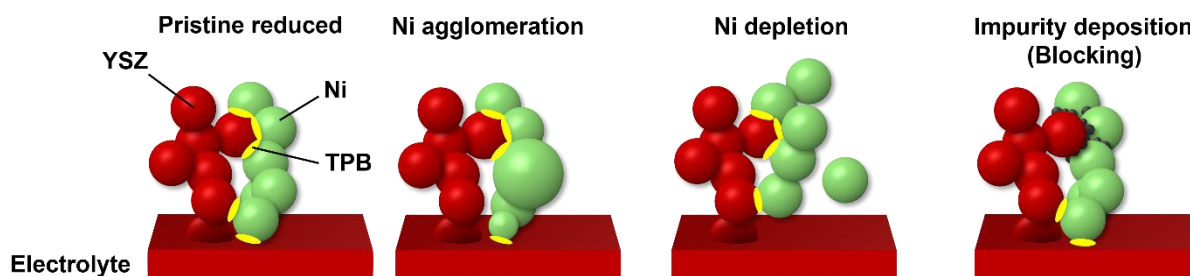


Figure 5 Degradation mechanisms occurring in Ni-YSZ fuel electrodes during SOEC operation.

3 Electrochemical Methods

3.1 Current Voltage Characteristics

3.1.1 Open Circuit Voltage

The open circuit voltage (OCV) is defined as the measured potential of an electrochemical cell when no current is flowing. Theoretically, the OCV equals the reversible (minimum) cell voltage derived from the Nernst equation. The Nernst equation for steam electrolysis in SOECs is given in Equation 3.1. and allows the calculation of the theoretical OCV for a specific gas partial pressure at the electrodes of the cell. Here, the commonly used activity of the reaction species is exchanged by the partial pressure p representing the gas mixtures used [38]. The theoretical OCV provides a way to assess gas leakages between the fuel and air electrodes in the SOC setup by comparing it with the measured OCV.

$$E_{Nernst} = \frac{\Delta G_f^0}{nF} - \frac{RT}{nF} \ln \left(\frac{p_{H_2O}}{p_{H_2} \sqrt{p_{O_2}}} \right) \quad (3.1)$$

3.1.2 Polarization Losses

The following fundamental knowledge and equations can be found in the textbook “Fuel Cell Fundamentals” in chapter 3 (activation losses) [39], chapter 4 [40] (ohmic losses) and chapter 5 [41] (concentration losses) if not otherwise referenced.

Under real operation conditions, various irreversible losses cause the required cell voltage for an electrochemical reaction to exceed the theoretical Nernst potential. The real cell voltage, E_{Cell} , results from the sum of the theoretical Nernst voltage and the respective overpotentials, as described in Equation 3.2.

$$E_{Cell} = E_{Nernst} + \eta_{Ohmic} + \eta_{Activation} + \eta_{Concentration} \quad (3.2)$$

The ohmic overpotential η_{Ohmic} follows Ohms law and is proportional to the current I with the resistance R as a factor as shown in Equation 3.3. The losses result from the resistance of the charge transport within the cells, including the electrodes, current collectors and general electrical contacts.

$$\eta_{Ohmic} = RI \quad (3.3)$$

The electronic contribution is due to electron transport, for instance, in the metal current collectors or the mixed ionic electronic conducting electrodes in the SOC. Normally, the electronic conductivity of the typically used materials is higher than the ionic conductivity. For

instance, the electronic conductivity of nickel (current collector) at 800 °C is in the order of $3 \cdot 10^4 \text{ S} \cdot \text{cm}^{-1}$, whereas the ionic conductivity of 8-YSZ (electrolyte) at 800 °C is in the order of 0.01 to $0.1 \text{ S} \cdot \text{cm}^{-1}$ [42-44]. Thus, the resistance caused by electronic transport is mostly negligible in a SOC. The ionic contribution arises from the transport of oxygen ions, which occurs via defects in the material structure. This mechanism typically involves ion hopping across vacancies or interstitial positions within the crystal lattice. The corresponding resistance is affected by the conductivity σ of a material as described in Equation 3.4, where A is the area and L is the length or the thickness of the electrolyte in the case of a SOC.

$$R = \frac{L}{\sigma A} \quad (3.4)$$

Activation overpotentials ($\eta_{Activation}$) are associated with the energy barrier of the electrochemical reaction that must be overcome. In the case of steam electrolysis, the half reactions shown earlier in chapter 2 (Equations 2.1 and 2.2) need a certain amount of energy. The needed energy is supplied by the voltage, increasing the theoretical OCV by $\eta_{Activation}$. The Buttlar-Volmer (BV) equation describes the relation between $\eta_{Activation}$ and the current density i and is shown in Equation 3.5. Here i_0 is the exchange current density, α the transfer coefficient as a measure of the symmetry of the energy barrier and n the number of exchanged electrons. The relationship shown here is under the assumption of a one step, one electron process ($n = 1$). In many multistep, multielectron transfers, the BV equation can still be a good approximation as the rate determining electron transfer is often a one electron process [45].

$$i = i_0 \left(\exp\left(\frac{\alpha n F \eta_{Activation}}{RT}\right) - \exp\left(\frac{-(1 - \alpha) n F \eta_{Activation}}{RT}\right) \right) \quad (3.5)$$

There are two limiting cases for the BV equation. At low overpotentials (or low current densities) where $\eta_{Activation} < \frac{RT}{\alpha F}$, a Taylor-MacClaurin expansion yields the linear approximation shown in Equation 3.6. At high overpotentials where $\eta_{Activation} > \frac{RT}{\alpha F}$, the equation simplifies to the Tafel Equation 3.7. in which b is the Tafel slope and α a constant [46].

$$i = i_0 \frac{\alpha n F \eta_{Activation}}{RT} \quad (3.6)$$

$$\eta_{Activation} = \frac{RT}{\alpha n F} \ln i_0 + \frac{RT}{\alpha n F} \ln i = a + b \ln i \quad (3.7)$$

Lastly, concentration overpotentials $\eta_{Concentration}$ contribute to the overall real cell voltage by taking into account limitations in the mass transport supporting the applied current. In the case of steam electrolysis in SOCs, steam must be transported to the electrode surface. The steam

molecules diffuse through the porous electrode structure to reach the internal catalytic active sites near the electrode/electrolyte interface. The diffusion inside the electrode is significantly slower than the external diffusion to the surface. When current is applied to the cell, the reactants are converted into products, as shown in Equation 2.3 for steam electrolysis. Consequently, a concentration gradient from the gas bulk phase (higher reactant and lower product concentration) over the porous electrode to the electrode/electrolyte interface (lower reactant and higher product concentration) is formed driving the diffusion. By the depletion of the reactant at the active catalytic sites the reaction rate is lowered and secondly, the Nernst potential is changed by the change in local gas composition (Equation 3.1.). These effects are significant at high currents where the conversion rate is high and diffusion to the active site is rate determining but are also present at lower current densities with minor impact on the operation voltage.

The concentration overpotentials due to diffusion limitations are described by Equation 3.8 where i_L is the limiting current density. i_L describes the situation where the reactant concentration at the catalytic active sites is zero. Thus, a further increase in voltage does not lead to an increase in current and the reaction is limited by diffusion. In Equation 3.9 the relationship of i_L to the effective reactant diffusivity D^{eff} , the reactant concentration in the bulk phase c_R^0 and the diffusion layer thickness δ (approximately the electrode thickness) is shown.

$$\eta_{\text{Concentration}} = \frac{RT}{nF} \left(1 + \frac{1}{\alpha} \right) \ln \frac{i_L}{i_L - i} \quad (3.8)$$

$$i_L = nFD^{eff} \frac{c_R^0}{\delta} \quad (3.9)$$

Concentration overpotentials by conversion limitations arise due to the gradual consumption of reactants along the gas channel which results in a decrease in educt concentration downstream. This effect is not discussed in detail in the present work, as it is not believed to be relevant to the experimental setup employed with low conversion rate and high gas flow rates (see chapter 5). For a comprehensive description of conversion related concentration overpotentials, the reader is referred to [47-48].

3.2 Electrochemical Impedance Spectroscopy

The fundamental principles and equations presented in this section are derived from the references [49] and [50].

Electrochemical impedance spectroscopy (EIS) is a frequency domain characterization method that uses a small amplitude alternating voltage or current signal. It enables the deconvolution of individual electrochemical processes according to their characteristic time constants in a time dependent system. These processes can include charge transfers,

adsorption/desorption phenomena, and mass transport (e.g. diffusion), and can be described by idealized electrical components such as resistors, capacitors, and inductors. Unlike a resistor which exhibits time independent behavior, components like capacitors and inductors are inherently time dependent and do not obey Ohm's law in the time domain. Instead, their voltage current relationship involves differential equations. By transforming these relationships into the Laplace domain using a complex frequency variable s , an Ohm's law like expression becomes applicable. The complex counterpart of the resistance is referred to as impedance $Z(s)$, which relates the complex voltage $V(s)$ to the complex current $I(s)$, as shown in Equation 3.10.

$$V(s) = Z(s) \cdot I(s) \quad (3.10)$$

Performing an EIS measurement typically involves the application of a small amplitude, periodic potential or current perturbation to excite the electrochemical system. Normally, a sinusoidal wave is applied due to mathematical ease of use. The system's response (either current or voltage) is recorded and exhibits a phase shift θ relative to the input signal. In Equation 3.11 an expression of an applied sinusoidal voltage is given to excite a system. In Equation 3.12 the resulting current response is displayed. In the equations, the angular frequency ω is included which is related to the frequency f by Equation 3.13. Applying a Fourier transformation enables both the input and response signals to be expressed in the frequency domain. The periodicity of both signals leads to the Fourier transformation not containing a real part in its transform variable resulting in the complex frequency being $i\omega$. The impedance $Z(i\omega)$ is calculated from the magnitude of the sine waves V_0 and I_0 and the phase shift θ as shown in Equation 3.14. The derived complex exponential function is transformed by applying the Eulers relation into a real and imaginary part as shown in Equation 3.14.

$$V(t) = V_0 \sin(\omega t) \quad (3.11)$$

$$I(t) = I_0 \sin(\omega t + \theta) \quad (3.12)$$

$$f = \frac{\omega}{2\pi} \quad (3.13)$$

$$Z(i\omega) = \frac{V(i\omega)}{I(i\omega)} = \frac{V_0}{I_0} \exp(i\theta) = Z_0 e^{i\theta} = Z_0 [\cos \theta + i Z_0 \sin \theta] = Z' + iZ'' \quad (3.14)$$

A commonly used method for visualizing EIS data is the Nyquist plot, which presents the complex impedance in a two dimensional graph and allows for an analysis of the system. Each individual data point corresponds to a specific frequency, typically decreasing from left to right. A simple Nyquist plot including three individual distinct time constants is shown in Figure 6 where the negative imaginary part $-Z''$ is plotted against the real part Z' . The ohmic resistance

(R_Ω) is obtained from the high frequency intercept with the x -axis while the low frequency intercept reflects the total cell resistance. The polarization resistance (R_p) is calculated as the difference between R_Ω and the total resistance. R_p includes the contributions from the polarization losses described in section 3.1.2. excluding the ohmic losses which are attributed to R_Ω . It should be noted that measurement instabilities, parasitic impedances and insufficient frequency ranges can hinder accurate and meaningful interpretation of Nyquist plots [51]. Another commonly used representation is the Bode plot where the magnitude $|Z|$ or the phase shift is plotted against the logarithmic frequency. Different representations of EIS data can provide complementary insights into the electrochemical behavior of materials. For example, the Bode plot is useful for the detection of parallel electric responses in electro ceramic systems [52].

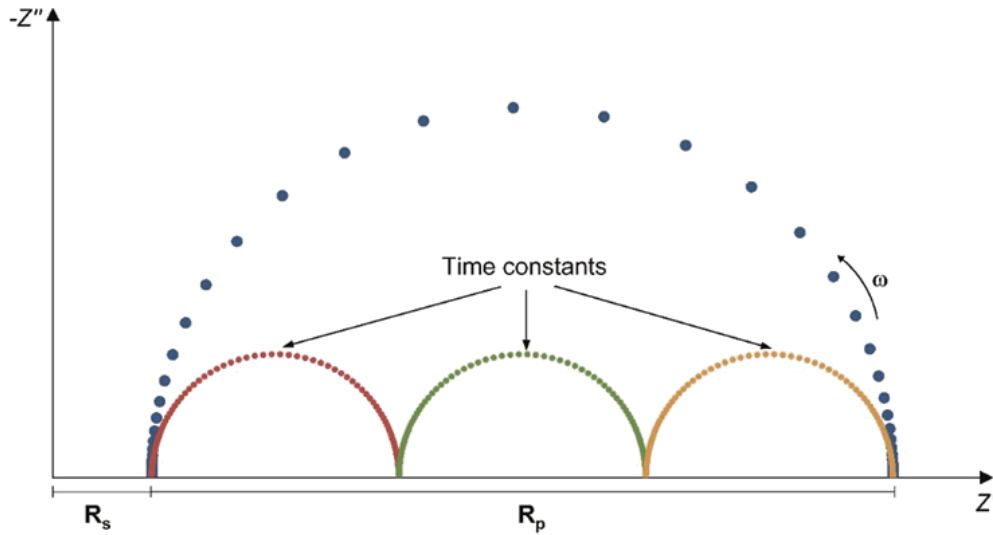


Figure 6 Nyquist plot including three individual three individual time constants and description of the ohmic and polarization resistance.

3.2.1 Equivalent Circuit Model

The analysis of EIS data commonly involves fitting an equivalent circuit model (ECM) to the recorded data. Such equivalent circuit models facilitate the deconvolution and interpretation of individual physicochemical processes occurring during electrochemical reactions. The most common elements employed in an ECM include resistors, capacitors or constant phase elements (CPEs) and inductors. These components are logically arranged, either in series or in parallel configuration depending on the specific characteristics of the investigated system (see Figure 7). The impedance of an ideal resistor, referred to as the resistance R_Ω , is frequency independent and purely real, given by Equation 3.15.

$$Z_{\text{ohm}} = R_\Omega \quad (3.15)$$

The impedance of an ideal capacitor is described by Equation 3.16 where C is the capacitance. The capacitor has no real impedance contribution and appears in a Nyquist plot as a vertical line in the negative imaginary direction ($-Z''$) direction.

$$Z_{\text{Capacitor}} = \frac{1}{i\omega C} \quad (3.16)$$

A basic ECM commonly used to describe the electrochemical interface in SOCs includes a resistor R_1 in series with an RC element composed of a resistor R_2 in parallel with a capacitor C_1 . In this configuration, the electrochemical double layer is described by the capacitor C_1 while the charge transfer at the electrode/electrolyte interface is represented by the resistance R_2 . The resistor R_1 reflects the ohmic resistance of the electrolyte. A schematic representation of the model is shown in Figure 7. The total impedance of the RC element is derived from applying Kirchhoff's circuit laws and corresponds to the combination of Equations 3.15 and 3.16 as expressed in Equation 3.17.

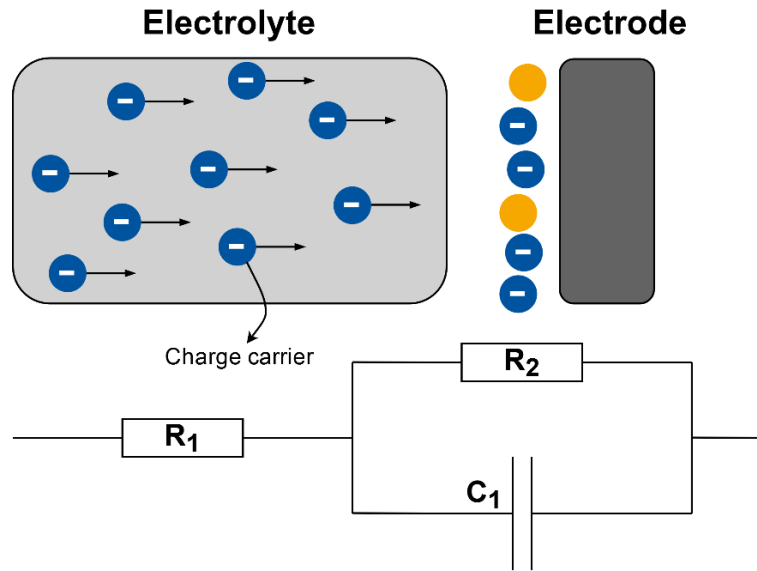


Figure 7 Exemplary circuit model referring to processes occurring in a SOC system.

$$Z_{\text{RC}} = \frac{1}{\frac{1}{R} + i\omega C} \quad (3.17)$$

Real electrochemical systems frequently deviate from ideal capacitive behavior due to material inhomogeneities, interfacial roughness, pore size distribution and anomalous diffusion mechanisms within the porous electrode network ^[53-54]. To account for these deviations, the capacitor in an RC element is often replaced by a constant phase element (CPE) as described by Equation 3.18. The exponent α , ranging between 0 and 1, characterizes the deviation from ideal capacitive behavior. A value of $\alpha = 1$ corresponds to an ideal capacitor, while $\alpha = 0$

represents an ideal resistor. Depressed semicircles in Nyquist plots are modelled by such RQ elements within the ECM.

$$Z_{RC} = \frac{1}{\frac{1}{R} + (i\omega)^\alpha Q} \quad (3.18)$$

Lastly, the impedance of an inductor is shown in Equation 3.19 with L being the inductance. Generally, an inductor is a reversed capacitance resulting in a straight line in the Z'' direction.

$$Z_{Inductor} = i\omega L \quad (3.19)$$

3.2.2 Distribution of Relaxation Times

Another approach for analyzing EIS data is the distribution of relaxation times (DRT) which provides a model free method for the deconvolution of EIS signals from the frequency domain into the time domain. The complex impedance is expressed as an infinite series of RC elements in series with a resistor, as shown in Equation 3.20 [55].

$$Z(i\omega) = R_\Omega + \int_0^\infty \frac{h(\tau)}{1 + i\omega\tau} d\tau \quad (3.20)$$

By normalizing Equation 3.20 using Equation 3.21 the polarization resistance R_p becomes explicit, as shown in Equation 3.22 [56-57].

$$\int_0^\infty g(\tau) d\tau = 1 \quad (3.21)$$

$$Z(i\omega) = R_\Omega + R_p \int_0^\infty \frac{g(\tau)}{1 + i\omega\tau} d\tau \quad (3.22)$$

The numerical computation of $g(\tau)$ is performed by discretization of the integral into a finite sum, where n is the number of times constants used (Equation 3.23).

$$Z(i\omega) = R_\Omega + R_p \cdot \sum_{k=1}^n \frac{g(\tau_k)}{1 + i\omega\tau_k} \quad (3.23)$$

A DRT plot is generated by plotting $g(\tau_k)$ against the relaxation time or the corresponding frequency. In the representation, ideal RC elements appear as distinct Dirac pulses at specific relaxation times or frequencies. By contrast, RQ elements typically used for describing real systems may not transform into distinct Dirac pulses but rather broader, asymmetric peak shapes. When the exponent α is below 1 these asymmetries cannot be captured by a single peak; instead the DRT transformation approximates the asymmetrically distributed response by several Gaussian peaks [58].

3.2.3 Application for Solid Oxide Cells

Both the fitting of EIS data to an ECM and DRT analysis are widely applied in SOC research to investigate performance improvements and degradation phenomena. For Ni-YSZ fuel electrode cells with LSCF or LSC air electrodes, several studies reported ECMs comprising four elements corresponding to at least four peaks observed in the DRT for atmospheric oxygen content at the air electrode ^[31, 59-61]. Analysis of the resistances derived either from DRTs or ECMs enables the assignment of individual electrochemical processes occurring in SOCs to specific relaxation frequencies. In Table 1 the assignment of processes for Ni-YSZ based cells is summarized with their respective relaxation frequencies. Such assignments are particularly valuable to investigate degradation, as they allow EIS data recorded before, during and after the stability test to be correlated with post test microstructural analyses at the end of the experiment. For instance, an increase in the high frequency processes was connected to a depletion and/or agglomeration of Ni in the Ni based fuel electrodes ^[31]. However, clear identification of specific processes remains challenging. As shown in Table 1, different groups attributed either process P₂ or P₁ to the Ni-YSZ fuel electrode charge transfer. Furthermore, sometimes both processes are described as coupled rather than distinct ^[59].

Table 1 Processes and their assignment from literature sources for Ni-YSZ based fuel electrode supported SOCs at an oxygen content of 21 % at the air electrode.

Process	Relaxation frequency (Hz)	Process assignment	Comments
P ₄	0.1 - 100	Ni-YSZ fuel electrode: Gas diffusion ^[31, 59-61] Gas conversion ^[60, 62-63]	Depending on the test setup geometry, gas diffusion or conversion is dominant. Sometimes both processes are present ^[60] .
		Air electrode: Oxygen surface exchange kinetics and O ²⁻ diffusivity in the bulk ^[59] Electrochemical process ^[60] Reaction and solid state diffusion ^[62]	
P ₃	10 - 100		
P ₂	100 - 8000	Ni-YSZ fuel electrode: Charge transfer reaction ^[61, 63] Fuel electrode transport ^[62]	Often both processes are donated as coupled fuel electrode

P₁

1000 - 50000

Ni-YSZ fuel electrode:

Charge transfer ^[62]

Ionic transport in the YSZ matrix

^[61]

processes or

electrochemical

reaction processes ^{[59-}

60]

4 State of the Art

Solid oxide fuel cells (SOFCs) have been a subject of extensive research for decades. Building on this foundation, solid oxide electrolysis cells (SOECs) have moved into as a promising technology. The high efficiencies make SOECs an especially interesting choice for producing hydrogen by electrolysis ^[19]. Several companies already offer SOEC systems commercially, and the planned installation of a 2.6 MW_{el} high temperature electrolyzer as part of the MultiPLHY project was recently announced ^[64].

State-of-the-art SOECs comprise a cermet fuel electrode from nickel and yttria stabilized zirconia (YSZ). The electrolyte is predominantly composed of YSZ, while the air electrode consists of a mixed ionic–electronic conducting perovskite, with lanthanum strontium cobaltite (LSC) and lanthanum strontium cobalt ferrite (LSCF) as prominent examples. A gadolinium doped ceria (GDC) barrier layer is commonly applied between the air electrode and electrolyte to prevent detrimental reactions that could compromise stability. Consequently, state-of-the-art SOECs are largely based on abundant and cost effective raw materials ^[19, 65].

One major research topic for the further implementation of SOECs concern stability issues which must be tackled ^[21]. Efforts focus particularly on developing more durable fuel electrodes through microstructural optimization or the design of new materials. As Ni agglomeration and migration within the Ni based fuel electrodes are common degradation mechanisms, the investigation of Ni free fuel electrodes has emerged as a promising strategy ^[66-67]. Significant progress in durability has already been achieved, with reported reductions in degradation rates by up to a factor of 100 ^[19]. Consequently, the scale up and techno economic assessment of SOECs for hydrogen production have recently been discussed in the literature ^[68-71].

With the scale up of SOECs and other electrolysis technologies, another challenge arises as hydrogen production not only requires electricity but also substantial amounts of water ^[2]. For 1 kg of H₂, at least 9 L of water is necessary, and it must be available at the location of the electrolyzer ^[72]. Additionally, current technologies predominantly rely on freshwater sources ^[2]. For instance, in Germany, an additional 3300 m³/s of freshwater would be required by 2050 to meet the demand for the planned hydrogen economy, as illustrated in Figure 8 ^[73-74]. This dependency could become problematic, as in the current decade the water demand is expected to rise due to the population growth, increasing incomes, and urban expansion ^[3-4]. In addition, water supply and availability is expected to become more erratic and uncertain, exacerbating water scarcity and stress ^[4].

In consequence, water scarcity among the urban population is projected to rise from one third (approximately 933 million people) to nearly half (1.7 – 2.4 billion people) ^[5]. Thus, competition between freshwater use for industrial and economic purposes and the need to meet the basic water demands of local populations is likely. As a result, the utilization of seawater in

electrolysis has moved into focus as a strategy to alleviate pressure on freshwater resources [8, 75].

Two main solutions are discussed in literature which include (i) the direct utilization of seawater (one step electrolysis) and (ii) the coupling of an industrial mature seawater reverse osmosis (SWRO) system with an electrolysis plant (two steps electrolysis) [76]. Some studies report that the direct use of seawater is advantageous due to additional devices such as the SWRO system requiring additional maintenance reducing the total operation time and thus the revenue [77-78]. Other studies argue that the two step electrolysis from seawater is preferable, as the costs of the SWRO system are marginal compared to the expenses of water, and it protects the electrolyzer from potential damage caused by impurities present in the seawater [75, 79]. For instance, in PEM electrolysis systems saltwater ions can damage the membrane and the electrode [8, 80]. However, a one size fits all solution must always be seen carefully taking into account plant size, geographic location, and technological maturity [81].

Another avenue, scarcely addressed in the literature, is the direct use of industrial and chemical wastewater as feedstock for electrolysis. Even in the food industry, significant sodium chloride concentrations are found in wastewater from processes such as meat curing, vegetable pickling, and fish processing [82]. In addition, numerous chemical industries discharge wastewater with a high content of sodium chloride (10 to 22 wt. %) or sodium sulfate (Na_2SO_4) [83-85]. For instance, polycarbonate synthesis generates wastewater with approximately 10 wt. % NaCl content [85]. Here the utilization of wastewater could support a circular economic approach, as illustrated in Figure A 1, and help minimize operational costs.

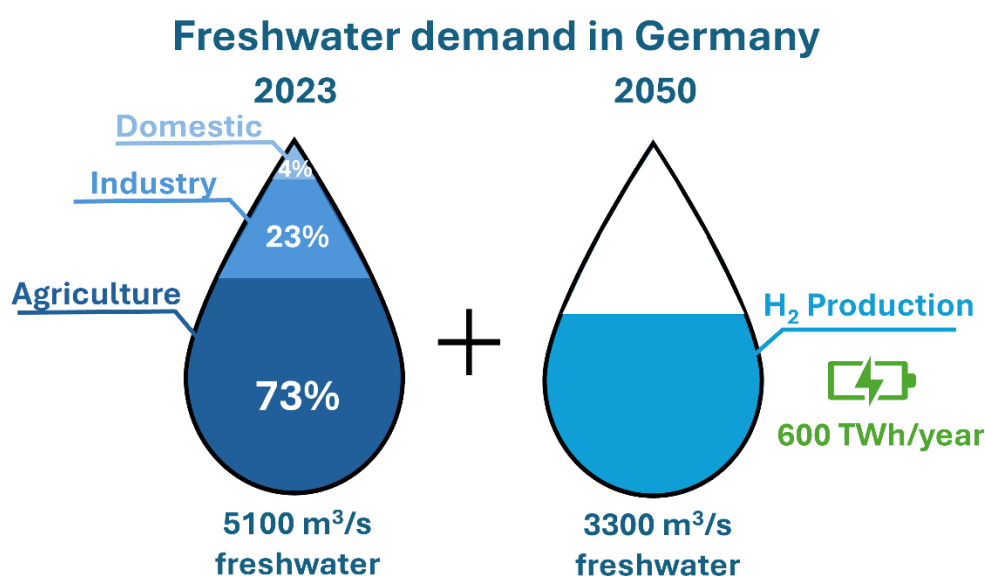


Figure 8 Freshwater demand in Germany in 2023 and the expected needed freshwater demand for hydrogen production equal to 600 TWh/year by 2025. The figure is based on [73].

In most evaluation studies on seawater utilization for hydrogen electrolysis, the focus has been on low temperature systems such as alkaline electrolysis, PEM, and AEM technologies. By contrast, SOEC systems are largely absent from technical and economic assessments. In SOECs, a steam generator is necessary, and the steam produced is used as feed gas. This inherently avoids the chloride evolution reaction commonly observed in other electrolysis systems. In the case of direct seawater or industrial wastewater utilization, a compatible steam generator system would be essential.

For instance, electrically heated steam generators are problematic when operated with seawater due to potential failure caused by salt cloaking. Thus, thermal water treatment could be advantageous when purification and steam generation are combined in one system ^[86]. Nevertheless, no thermal treatment and purification concept for continuous SOEC operation has yet been evaluated in the literature to the authors best knowledge. Direct seawater feeding into a thermal evaporation/purification system could be compared to a two step process in which first passes through a reverse osmosis (RO) before being evaporated in a conventional (electrical) evaporator. Even in such cases, trace amounts of impurities (at the ppm or ppb level), transported to the cell for example via aerosols in the steam, could still pose critical risks to the electrochemical reaction or the evaporators.

Chlorine, sulfur, and silicon containing salt or molecules are problematic. Silicon containing impurities can accumulate at the TPB of the Ni-YSZ fuel electrode leading to the passivation and degradation of the SOEC ^[87-89]. Sulfur containing impurities likewise cause fuel electrode passivation of the SOEC ^[90-91]. Additionally, studies on SOFC operation have examined the impact of halogens in the feed gas. Here especially, chlorine containing impurities in coal syngas (HCl and CH₃Cl) were investigated and found to harm the Ni-YSZ fuel electrode stability ^[34, 92-93].

Several studies have investigated the effects of direct seawater utilization on SOEC operation at the laboratory scale ^[9, 14-15, 94]. All studies used a bubbler setup for steam generation consisting of a heated water bath and carrier gas to transport the produced steam to the cell. One study examined the use of synthetic seawater with self fabricated Ni-YSZ/YSZ/LSCF-GDC fuel electrode supported single cells ^[9]. The authors reported no significant differences in the initial performance when comparing pure water and seawater operation, consistent with other studies ^[9, 14-15, 94]. Furthermore, similar degradation rates are observed for pure water and seawater operations. However, a total degradation time of only 120 hours was achieved, which is too low for a meaningful long term projection. In addition, the authors reported no salt depositions in the cross sections of the fuel electrode by scanning electron microscopy (SEM) imaging. However, neither energy-dispersive X-ray spectroscopy (EDX) analysis nor investigation of the surface of the fuel electrode was applied.

Another study reported no impact on the stability of a Ni-YSZ fuel electrode cell during a 400 hour degradation test; however, no comparison to a pure water measurement in the same test setup is reported ^[14]. Furthermore, sea salt deposition inside the inlet pipe of the SOEC is detected, which could be due to insufficient isolation of the inlet pipes, and would explain the high voltage oscillations during the stability test ^[14]. Furthermore, no salt deposits were found by SEM imaging.

A recent study from 2023 reported a stability test over 1000 hours of operation with direct seawater utilization ^[15]. They reported a degradation rate of $129 \text{ mV}\cdot\text{kh}^{-1}$ for a gas composition of 67 % H_2O + 33 % H_2 for Ni-YSZ/YSZ/GDC/LSCF-GDC cells at 750°C and a current load of $300 \text{ mA}\cdot\text{cm}^{-2}$. Their reference pure water measurement was performed for only 150 hours and showed a higher degradation rate of $213 \text{ mV}\cdot\text{kh}^{-1}$. The study does not further explain the differences between seawater and pure water. The seawater operated cells were post characterized by SEM-EDX analysis and no impurity deposition was detected. However, the EDX mapping was done in a big area of around $60\cdot60 \mu\text{m}$; thus, small particles could be overseen. Furthermore, no EDX map of Na impurities is shown even though the Na content in seawater is the highest among the contained cations ^[95].

Another study from 2023 reported a stability test of Ni-YSZ pellets at 750°C for 500 hours of operation time and measured the conductivity ^[94]. Again, no reference data was recorded during the measurement to compare seawater and pure water under the current load. However, the authors reported a comparison of the ASR evolution as a measure for the conductivity at no current load for seawater and pure water where seawater operation led to a higher degradation rate of $0.0072 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$ compared to $0.00084 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$. They stated that seawater steam caused agglomeration and loss of Ni particles in the Ni-YSZ support. Furthermore, they stated that no impurities were found by SEM-EDX analysis, even though only the EDX maps of the elements Ni, Zr, O, Y and B are shown in the manuscript. In addition, the EDX mapping was done for a large area of around $60\cdot60 \mu\text{m}$.

In the author's opinion, several issues can be identified in the current laboratory scale literature, as discussed above. Either insufficient post test characterization, insufficient comparison with pure water reference measurements or short degradation times limit the significance of the reported findings. Furthermore, there is a lack of laboratory stability studies involving wastewater or saline water with higher salt concentrations either for investigating industrial wastewater utilization or as accelerated stress tests for seawater operation. In addition, comprehensive technical and economic analysis of seawater utilization in SOECs has yet been published to the authors' best knowledge.

Against this background, the present thesis aims to study the effects of direct saltwater and seawater operation in SOECs. First, the transport of impurities, including salts, to the cells is investigated. Second, the impact of the direct use of this water on the performance and stability

of SOECs is discussed. This helps to point out possible critical impacts which will help to discover the feasibility of seawater and wastewater utilization, a deeper understanding and the possibility to prevent or improve the operation. Thirdly, a novel system concept is evaluated, focusing on a technically feasible approach for simultaneous thermal evaporation and purification in a real SOEC plant's continuous operation with seawater. Finally, a technical and economic assessment of seawater utilization at larger scales is carried out, comparing the proposed concept with a seawater reverse osmosis (SWRO) system coupled to an SOEC. The research concept and context of the thesis are graphically shown in Figure 9.

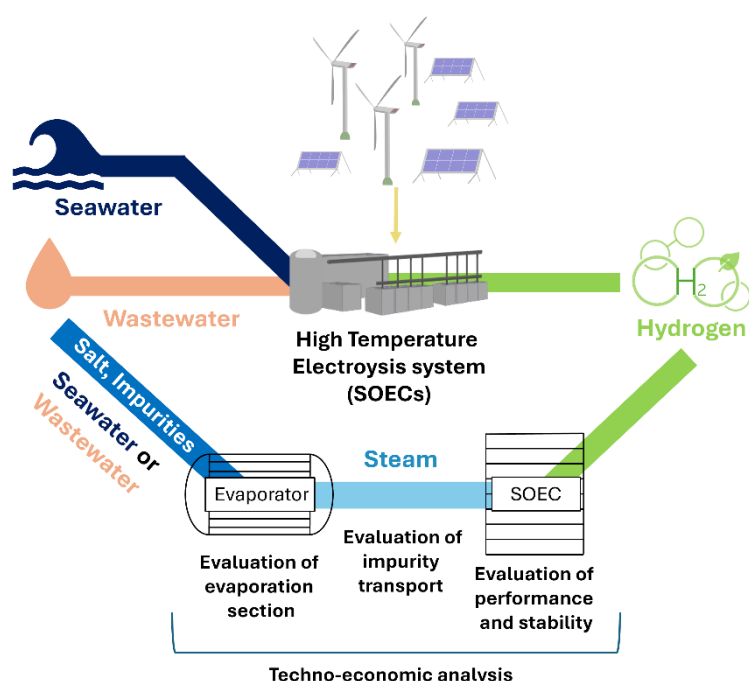


Figure 9 Graphical representation of the thesis research and development with the research questions.

5 Experimental

5.1 Measurement Setup

A schematic display of the electrochemical measurement setup is shown in Figure 10. Mass controllers (MFCs) by Bronkhorst GmbH (Germany) were used to control the gas compositions and flows on the air and fuel electrode channels. These were factory calibrated to standard liters per minute (SLM) at 20 °C and 1 atm. For the fuel electrode, dry H_2 and N_2 were primarily used in the experiments; however, CO and CO_2 mass flow controllers were also installed. At the air electrode O_2 , N_2 and air gas flows are possible. Steam is added to the fuel electrode gas by leading the dry fuel gases through a heated water bath. The steam content is adjusted by the temperature depending on water vapor pressure over an oil heated condenser. The water in the bubbler was exchanged depending on the investigated water. For the baseline pure water measurements, the bath was filled with deionized ultrapure water. For the investigation of seawater, real seawater gathered at the island Texel in the Netherlands was used. In Table A 1, the salt composition of the seawater is shown as determined by ICP-OES (iCAP 7600, Thermo Fisher Scientific, Germany) performed by ZEA-3 of Forschungszentrum Jülich. In the case of the saturated NaCl solution, the salt was added to deionized ultrapure water. For salt containing solutions, the water bath temperature was increased to account for the elevated boiling point.

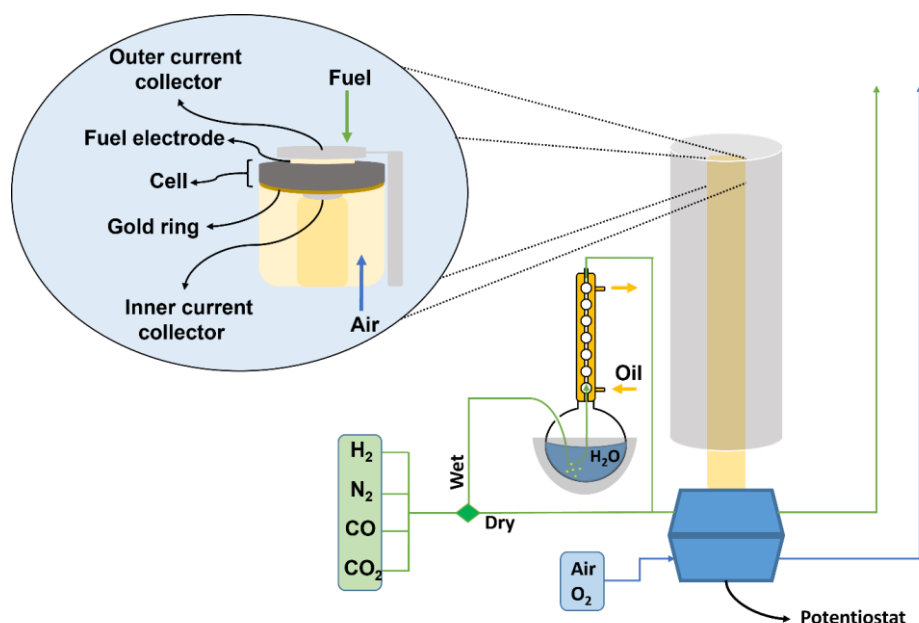


Figure 10 Schematic illustration of the used measurement setup.

The solid oxide electrolysis cell was placed in a Probostat test cell setup. The cell was contacted by a platinum mesh on the air electrode side and a combined nickel and platinum

mesh on the fuel electrode to minimize Seebeck effect–related measurement artifacts. The individual fuel and air gas chambers were sealed with a gold ring placed between the cell and the ceramic sample holder. The cell is fixed and gas tightened by a spring loaded ceramic tripod. A Faraday cage surrounded the setup to prevent electromagnetic interference. A Vertex potentiostat of the company Ivium Technologies B.V. (The Netherlands) is used for electrochemical measurements.

5.2 Electrolysis Cell

The solid oxide electrolysis cells used in this study were commercially bought from the company Elcogen AS (Estonia). The cells were supplied as fuel electrode supported single button cells with a diameter of 2 cm and an active area of 0.79 cm². Each cell consists of a Ni-YSZ fuel electrode (NiO-YSZ before reduction) which is divided into the more porous support and the denser active functional layer (AFL) adjacent to a thin 8YSZ electrolyte. Above the Ni-YSZ fuel electrode, a thin Ni contact layer is applied. The air electrode side consists of a GDC barrier layer and a LSC air electrode. The complete cell design is schematically displayed in Figure 11. The manufacturer provided thickness data for the Ni–YSZ fuel electrode, the YSZ electrolyte, and the LSC air electrode, whereas the thicknesses of the Ni contact layer and the GDC barrier layer were determined by the author via secondary electron microscopy (SEM) imaging. Two production batches of cells, referred to as the 'new' and 'old' batches, were used throughout the study. Table A 2 in the appendix lists the tested cells from each batch used for the stability experiments.

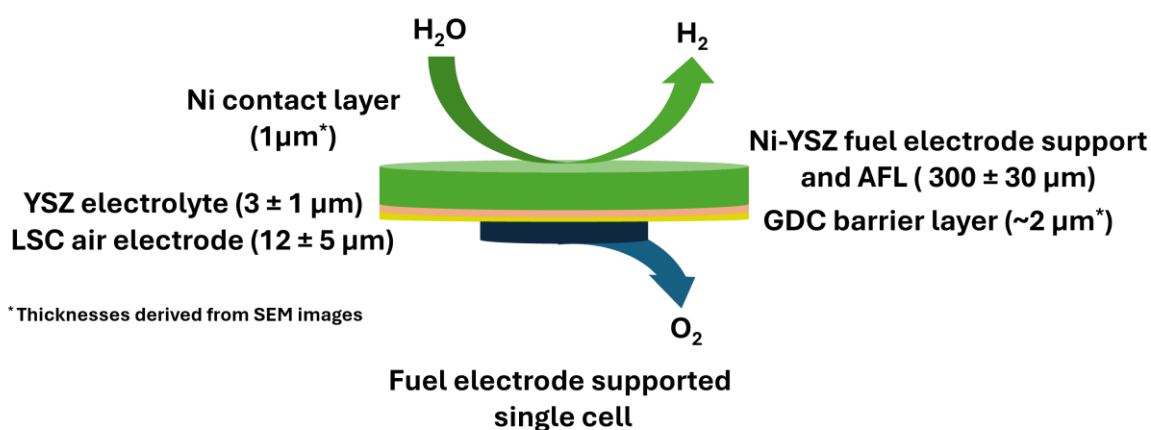


Figure 11 Schematic representation of the used Ni-YSZ fuel electrode single cell with a total diameter of 2 cm.

5.3 Electrochemical Characterization

To reduce the NiO-YSZ fuel electrode, the cell was treated with H₂ at 900 °C. Heating to 900 °C was carried out under a flow of 6 L·h⁻¹ N₂ at the fuel electrode and 6 L·h⁻¹ air at the air electrode with a heating rate of 1.5 °C·min⁻¹. The reduction was done stepwise with gas compositions and time frames shown in Table 2. Air was supplied during the reduction at the air electrode. Each gas composition was kept until the OCV remains constant. After the reduction, the cell's performance was evaluated to ensure proper contact and no faultiness of an individual cell. A current density voltage curve (iV) curve measurement in fuel cell mode was conducted from OCV down to 0.6 V and back to OCV at 900 °C. Only cells achieving a current density of at least 3 A·cm⁻² at 0.6 V were used for the subsequent measurements shown in this thesis.

Table 2 Reduction procedure with respective flow rate at fuel and air electrode

Step	N ₂ (L·h ⁻¹)	H ₂ (L·h ⁻¹)	Air (L·h ⁻¹)	Time
1	6	0.5	6.5	2 - 6 hours
2	6	1	1	1 - 2 hours
3	6	2	2	30 - 60 min
4	6	3	3	30 - 60 min
5	5	4	4	30 - 60 min
6	4	5	5	30 - 60 min
7	3	6	6	30 - 60 min
8	2	7	7	30 - 60 min
9	1	8	8	30 - 60 min
10	0	9	9	15 - 30 min

The shown iV curve measurements in the thesis were performed by potentiostatic cycling from OCV to 0.6 V to 1.4 V to 0.6 V to OCV with a scan rate of 10 mV·s⁻¹. EIS measurements are recorded in a frequency range from 0.11 to 114 kHz with 25 data points per frequency decade and an amplitude of 20 mV to 50 mV, depending on the linearity of the system. Before each measurement, an equilibration time of at least 60 seconds was maintained. The EIS data were evaluated using the commercial analysis software RelaxIS by RHD-Instruments GmbH & Co. KG (Germany). The DRT is calculated using the same software by Gaussian discretization. The DRT plots were prepared following the procedure described by Hahn et al. ^[96]. The current and resistance derived from iV curves and EIS measurements were normalized by the active area of the cells. iV curves and EIS measurements were conducted at various operating conditions under the utilization of different waters such as pure water, seawater and concentrated sodium chloride solution.

In case of a temperature variation, iV and EIS measurements were recorded at seven temperatures in the range from 750 to 900 °C in steps of 25 °C. The gas compositions at the fuel electrode were constant at 60 % H₂O + 40 % H₂ for all the measurements.

In case of a steam content variation at the fuel electrode, the operating temperature was held constant at 800 °C and H₂ was used as balance gas. The steam variation was in the range of 10 to 60 % H₂O.

The investigated short term stability tests were performed at a constant voltage of 1.25 V for a total measurement time of 212 hours. The tests were performed under different operating conditions. The operating temperature evaluation was performed at three temperatures of 750, 800 and 850 °C with a constant gas composition of 60 % H₂O + 40 % H₂. For the variation of steam content at the fuel electrode three conditions with 60, 50 and 40 % H₂O with H₂ as balance gas at 800 °C were investigated.

The long term stability measurements were performed at a constant current density of $-1 \text{ A}\cdot\text{cm}^{-2}$, 800 °C and with a gas composition of 60 % H₂O + 40 % H₂ at the fuel electrode for 500 to 1000 hours of operation. All measurements were performed with a total gas flow rate of $9 \text{ L}\cdot\text{h}^{-1}$ at both electrodes. At the air electrode atmospheric air was used. During the stability measurements, electrochemical measurements including iV curves and EIS measurements were performed every 100 hours at OCV. Here, the stability measurements were stopped and restarted.

The cooldown of the cells to room temperature was done with a gas composition of $0.5 \text{ L}\cdot\text{h}^{-1} \text{ H}_2 + 6 \text{ L}\cdot\text{h}^{-1} \text{ N}_2$ at the fuel electrode and $6 \text{ L}\cdot\text{h}^{-1}$ air at the air electrode with a cooling rate of $1.5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

5.4 Post characterization

The degraded cells were post characterized by various techniques after dismantling them by hand from the measurement setup and exposure to air atmosphere.

The surface of the Ni-YSZ fuel electrode was characterized by X-ray diffraction (XRD) at room temperature using a PANalytical X'pert MPD diffractometer (Malvern Panalytical), with Mo-K α or Cu-K α incident radiation. In the case of Mo incident radiation, a mathematical conversion to Cu-K α was done for better comparison with literature or previous results. The system was operated in a reflection transmission spinner configuration with a generator voltage of 55 kV and a tube current of 40 mA in the case of Mo-K α incident radiation. In the case of Cu-K α radiation a generator voltage of 40 kV and a tube current of 40 mA were applied. Grating incidence X-ray diffraction (GI-XRD) further characterized the surface of the fuel electrode at room temperature an identical instrument with Cu-K α incident radiation. The system was operated in a reflection transmission spinner configuration with a generator voltage of 40 kV and a tube current of 40 mA.

X-Ray Photoelectron Spectroscopy (XPS) measurements were performed on the fuel electrode surface of the degraded cells. A Phi5000 VersaProbe II (ULVAC-Phi Inc., USA) was used for the measurements. The Source was monochromatic Al K-alpha (1.486 keV). The X-ray setting was 50 W, 15 kV and 200 μm spot size. The Survey was recorded with 187.5 eV pass energy in 0.8 eV steps and a 100 ms/step scanning rate. The Quantification of elements was done in at% with Shirley-Background and with empirical relative sensitivity factors. The measurements and data analysis were done by the ZEA-3 of Forschungszentrum Jülich.

In the case of the degraded cell operated with steam from saturated sodium chloride solution, a plasma focused ion beam scanning electron microscope (TESCAN Amber X; TESCAN) was used for planar imaging. Secondary electron (SE) imaging was performed using the integrated Everhart-Thornley (E-T) detector and the multidetector (MD), while backscattered electron (BSE) imaging was performed using the MD detector only. A low acceleration voltage of 2 kV was used to enable surface specific resolution. Compositional analysis was performed using energy dispersive X-ray spectroscopy (EDX) using the Elite Super detector from EDAX. Data acquisition and analysis were performed using EDAX Apex Advanced software (version 2.5.1001.0001). The same instrument was used for the EDX analysis of the polished and embedded cross sections investigating the Ni and Zr phases of all shown cells with a higher acceleration voltage of 20 kV. The analysis and segmentation of the SEM/EDX images presented were done using Python, as described in ^[97]. These results were conducted in cooperation with Jean Pierre Puc and Pritam Chakraborty under the supervision of Dr. Basak at IET-1.

The other shown surface measurements were performed by the author using a Quanta FEG 650, FEI® with the same operating parameters as discussed above. The same instrument was used for fractured cross section characterization for all cells. A low acceleration voltage of 2 kV was used to enable surface specific resolution. Compositional analysis was performed by EDX using the Elite Super detector from EDAX with a higher acceleration voltage of 20 kV. Data acquisition and analysis were performed using EDAX Apex Advanced software (version 2.5.1001.0001). Additionally, the instrument was used to detect Si impurities in the Ni phase with an acceleration voltage of 20 kV.

5.5. Techno-Economic Analysis

5.5.1 Implementation in Aspen Plus

The commercial software Aspen Plus, with its extensive thermodynamic and physical properties database, is used for the implementation and simulation. This approach is time efficient for running chemical process studies and system modeling, integration, and

optimization. The Aspen Plus flow sheets used in this thesis can be found in Figure A 11 and Figure A 12.

For easier implementation, the salt content in seawater was simplified to 3.5 mol% NaCl. The energy consumption of auxiliary equipment (e.g., magnetic valves, sensors, and microprocessors) is not accounted for in the flowsheets, and the compression and storage of product gases are not included. A pressure drop of 2 % for the steam generation and the SOEC stack is assumed to account for minor hydrogen losses. The heat exchangers are modeled as counter flow shell and tube systems. The efficiencies of the balance of plant components retrieved from literature are shown in Table A 3 in the appendix ^[98-99]. The process is modeled in Aspen Plus using the ELECTRN and Peng-Robinson property methods. The thermodynamic behavior of seawater was modeled using the ELECTRN property method. The Peng-Robinson method is used after the point where no significant salt concentrations remain in the system. The mentioned cyclic streams were implemented as tear streams in Aspen Plus. The recycle stream of the H₂ was defined as a design specification to be maintained at 10 mol% of the feed stream to the SOEC system to prevent reoxidation of the Ni based fuel electrodes. The required molar flow of generated steam is adjusted by the design specification for the water vapor to ensure a steam utilization of 85 % and the prevention of excessive steam production. The falling film evaporator (FFE) is modeled with a heater and a flash block. Python unit operations represent the SOEC stack and the seawater reverse osmosis (SWRO) unit. Compressors are added to the process (not present in the simplified flowsheets) to compensate for the pressure losses in the SOEC stack. Here, it is important to note that the heat exchangers shown in the Aspen flowsheets (Figure A 11 and Figure A 12) do not reflect their actual positions. Their precise number, positions, and heat sources are determined after optimization in the Aspen Energy Analyzer.

Since Aspen Energy Analyzer cannot interpret Python based unit operations in terms of direct thermodynamic or energy analysis, the SOEC and SWRO models were encapsulated within a hierarchy block in Aspen Plus. This allowed the specification of thermal and electrical energy demands as conventional stream connections, enabling proper integration into the energy analysis framework. A Hierarchy Block in Aspen Plus is a specialized sub flowsheet that appears as a standard process block within the main flowsheet but contains an independent internal flowsheet with defined input and output flows. In this context, the Hierarchy Block serves to encapsulate Python based models (e.g., SOEC and SWRO) while explicitly defining their mass and energy flows as inlet and outlet streams. A more detailed description about the use of Python Unit Operations can be found in the official Aspen Plus user guide and in ^[100]. In addition, a starting stream with a small amount of H₂ is fed into the process and removed at the end to ensure convergence in Aspen Plus.

5.5.2 Modeling of the System Components

The Solid Oxide Electrolysis Cell (SOEC) was modeled as a steady state, zero dimensional white box unit, capturing its electrochemical and thermodynamic behavior through first principles equations implemented in Python. The model assumes no time dependent changes in the operation and transient dynamics e.g. heat up and shut down are not considered. The model was executed using AmsterChem's 'Python Unit Operation'- a CAPE-OPEN-compliant interface enabling seamless integration of custom Python based unit operations into a process simulation environment. This setup allowed for flexible and transparent modeling of the SOEC's mass, energy, and electrochemical balances. In Aspen Plus, a block with defined input and output streams refers to the model. It was assumed that the SOEC operated with a constant current of $-1 \text{ A}\cdot\text{cm}^{-2}$ and a pressure drop of 2 %. The respective input parameters are shown in Table A 5.

The falling film evaporator was modeled by a heat exchanger unit followed by a two phase flash unit. Here, an approach from the literature was adapted where a thin film evaporator was simulated using only unit operations in Aspen Plus ^[101]. Heating the seawater to its saturation temperature is done by hot utility fluid. The surface temperature, tube outer diameter, and chamber pressure determine the evaporation rate. This work assumed an evaporation rate of 50% ^[102]. The heater's output is a two phase mixture of water vapor and concentrated brine that is not reflective of the real process ^[101]. A slash unit separates the mixture into concentrated brine and water vapor. The separation happens without heat exchange. A pressure drop of 2 % is assumed for evaporator pressure losses ^[99]. The salt contents in the resulting vapor are considered negligible since the vapor pressure of salt is low. In the actual process, a demister is installed downstream of the evaporator ^[103-105].

Based on the SIRION Sea Water Reverse Osmosis System D-75 by Veolia, the SWRO unit was simplified and modeled as an isothermal, steady state gray box model using the Python Unit Operation plugin from AmsterChem ^[106]. The seawater feed is assumed to be at 20 °C and a pressure of 5.5 bar entering the SWRO. The output pressure of the SWRO unit is set to 1.1 bar. The separation of high salinity retentate and low salinity permeate is done in the SWRO, where the retentate is discharged as waste. The system operation parameters shown in Table A 4 in the appendix are integrated into Python and a mass balance was added ^[107]. The energy consumption is calculated using the feed pump and the SWRO unit.

5.5.5 Optimization of the Heat Consumption

The heat integration is done using the Aspen Energy Analyzer, which includes heat recovery and improving heat integration in the system. An analysis determining where heat is required and integrated was performed at first. In both cases, the water entering the evaporator (FFE: seawater and SWRO: pure water) can be preheated to a temperature of 90 °C in a

preheater ^[102]. A higher temperature is critical due to the flash effect before the evaporator. In the case of the FFE, the heat removed from the brine stream can be used to preheat the seawater. After the evaporator, the steam must be superheated to a minimum of 116.6 °C to prevent condensation ^[108]. This work sets a temperature of 130 °C to provide safety against condensation. The steam is heated to an operating temperature of 800 °C after compression. After the SOEC unit, a heat exchanger is integrated into the oxygen flow system to keep the sweeping gas at 800 °C. Cooling is limited to 30 °C after the heat integration as further compression of the product gases is not considered.

A heat exchanger network was created in the Aspen Energy Analyzer. Specified constraints are separating H₂ and O₂ streams in the same heat exchanger due to safety constraints. The number of individual connections between the cold and hot streams determines the number of heat exchangers. Using a minimum temperature difference of 10 K, a composite curve is generated based on the process streams.

5.5.6 Techno Economic Assessment

A comparison is made for the two described seawater utilization cases (FFE/SOEC and SWRO/SOEC) and a conventional SOEC system using freshwater. Here, the freshwater price is included. The levelized cost of hydrogen (LCOH) was calculated for all cases. A sensitive analysis was performed taking into account electricity, external heat and freshwater prices ^[109]. The calculation of the LCOH was done using Equation 5.1 based on the methodology in literature where a conventional SOEC system using deionized water as feed was evaluated ^[109]. In Equation 5.1 the CAPEX relates to the one time **capital expenditure**, and OPEX to the sum of the discounted **operational expenditure** and n the system lifetime in years. Moreover, r is the discount rate and m_{H_2} the produced mass of hydrogen.

The system's lifetime is set to 20 years, with the first year being the construction year. The operation time is set to 8000 hours per year. The system degradation rate (SDR) is considered by periodic replacement of the stacks where the costs are included in the OPEX. The service and maintenance costs are 2 % of the CAPEX for the conventional case and 4 % for the seawater cases ^[109]. All costs are presented in US dollars based on the current exchange rate of September 2024. This work adjusts the LCOH and components to the German market. The electricity costs are based on the current German electricity market price of 89.55 USD/MWh. The cost of deionized water is set to 0.01 USD/kg while the cost of seawater is considered zero ^[109]. Costs associated with other operational activities are assumed to be 1 % of the CAPEX. The personnel costs are based on the average German salary for full time employees, which is 58 USD/year. The cost of low pressure steam is given as 20 USD/Mt for Germany. The transportation costs of external heat are estimated at 8.4 USD/MWh ^[110]. A detailed summary of the costs is provided in

Table A 6 to Table A 9 in the appendix. The processing of the product streams is considered in the techno economic assessment.

$$\text{LCOH} = \frac{\text{Total Lifetime Cost}}{\text{Total Lifetime H}_2 \text{ Production}} = \frac{\text{CAPEX} + \sum_{n=1}^N \frac{\text{OPEX}_n}{(1+r)^n}}{\sum_{n=1}^N \frac{m_{\text{H}_2}(1 - \text{SDR})^n}{(1+r)^n}} \quad (5.1)$$

6 Results and Discussion

The following chapters elucidate a scientific investigation of saline waters in laboratory scale SOECs and technical and economic analysis of seawater utilization in bigger scale SOEC systems. The results start with an investigation of degradation in pure water operation on a laboratory scale. In the following, the term pure water refers to ultrapure deionized water. Next, real seawater operation is evaluated in terms of initial performance and long term stability. Building on these results, the utilization of saturated sodium chloride solution is investigated under the same criteria. Finally, a technical and economic analysis for a 1 MW_{el} SOEC system operated with seawater is shown, including a system approach for efficient thermal evaporation and purification.

6.1 Stability in Pure Water Operation

In this chapter, the stability of state-of-the-art Ni-YSZ fuel electrode supported cells was investigated on the laboratory scale for two different production batches of SOC single cells (old and new). In the rest of the manuscript cells from the old production batch are identified by the subscript old and cells from the newer batch by the subscript new. In this chapter, pure water was used for the generation of steam. The term pure water is used within the chapters to describe ultrapure deionized water. Differences in individual operated cells were connected to degradation phenomena and mechanisms by electrochemical investigations and post test characterization techniques. This is important to enable a meaningful comparison of cells operated with different waters for steam generation on the laboratory scale. Therefore, stability tests at the same operation conditions and a current load of $-1 \text{ A}\cdot\text{cm}^{-2}$ are conducted for two production batches of SOECs used in the thesis. EIS and post test characterization clarify differences in degradation behavior. The shown stability measurements in the appendix at higher steam contents were conducted during the research internship of Chenlu Li ^[111]. The stability measurement for pure water cell 1_{old} was conducted during a supervised master thesis by Niklas Eyckeler ^[112]. The stability measurement for pure water cell 2_{old} was conducted during a supervised internship by Niklas Eyckeler ^[113]. The shown Ni-YSZ fuel electrode polished cross section SEM-EDX measurements were recorded in cooperation with Jean Pierre Puc and Pritam Chakraborty from the working group of Dr. Basak at IET-1 Forschungszentrum Jülich. In addition, some of the results shown here were published in ^[51, 114].

6.1.1 Long Term Stability Measurement

6.1.1.1 Operation Voltage Evolution

Firstly, the evolution of the voltage as a function of the operation time is discussed. Thus, Figure 12 shows the cell voltage evolution over time for individual Ni–YSZ electrode–supported SOECs operating at a temperature of 800 °C, a current density of $-1 \text{ A}\cdot\text{cm}^{-2}$ and a gas composition of 60 % H_2O + 40 % H_2 . As mentioned above, steam was generated from ultrapure water. Every 100 hours, the electrolysis operation was interrupted to perform EIS measurements at OCV and measure iV curves.

As listed in Table A 2, pure water cells 1_{old}, 2_{old} and 3_{old} belong to an older production batch, whereas pure water cells 4_{new} and 5_{new} come from a newer one. The cells from the newer production batch exhibit initial voltages of 1.062 V and 1.074 V. Initial voltages between 1.101 V and 1.17 V are recorded for the old production batch. Thus, the newer batch performs slightly better (40 to 100 mV) than the older one. The different initial voltage values are explained by the production and/or microstructure differences between the batches. However, differences between cells from the same batch are visible in an order of magnitude of 10 to 70 mV. Differences between the same production batch reflect slight differences in cell contacting or the use of different experimental setups. These differences must be considered when comparing the initial performance of cells within a production batch and between cells of the different batches.

Dips in voltage occur during the stability measurements every 100 hours, which are especially noticed after 300 hours of operation. The dips occur in both cell batches. These are expected to correspond to the EIS and iV curve measurements conducted as the constant current in SOEC operation is switched off when the cell is operated at OCV or in SOFC mode for the iV curve measurements. Similar spikes and drops in voltage were reported in the literature for switching between SOEC and SOFC mode suggesting a performance recovery [115-117]. A similar recovery is expected to take place in the cells used here. Since all cells experienced the same experimental protocol, these dips do not affect the overall degradation comparison. All cells exhibit a gradual voltage increase over time, but the shape of the degradation curve differs between production batches. The cells from the old production batch, pure water cell 1_{old}, pure water cell 2_{old}, and pure water cell 3_{old}, show a rapid rise during the first 200 h followed by a linear increase for the remainder of the test. A similar evolution is observed for cells tested at higher steam contents, as shown in Figure A 2 and in a previous study by our group [118]. The single cells from the new production batch, pure water cell 4_{new} and pure water cell 5_{new}, follow a steady, linear voltage increase throughout the measurement. Anomalous spikes in voltage around 580 hours of operation are due to a malfunction of the automatic water supply for steam generation. They are not believed to alter the overall degradation trend. Due to the

observed performance deviations, batch to batch comparisons under identical conditions are not meaningful, whereas within batch trends remain valid.

Overall degradation rates were calculated by subtracting the end voltage from the initial voltage and interpolating to 1000 h of operation, as shown in Table 3. Pure water cells 1_{old}, 2_{old} and 3_{old} exhibit degradation rates between 374 mV·kh⁻¹ and 564 mV·kh⁻¹ whereas pure water cells 4_{new} and 5_{new} show significantly lower rates between 147 mV·kh⁻¹ and 209 mV·kh⁻¹. Thus, higher degradation rates are observed for the older batch, which also exhibited higher initial voltages and a pronounced early voltage increase. These findings indicate that differences between the two batches are significant and that inter batch comparisons are not suitable for evaluating operational parameters affecting degradation behavior. An alternative approach commonly used in the literature involves linear fitting of the steady degradation period. Considering only the linear periods of degradation, degradation rates between 215 mV·kh⁻¹ and 227 mV·kh⁻¹ were observed for the cells of the old production batch. The new production batch exhibits degradation rate between 126 mV·kh⁻¹ and 186 mV·kh⁻¹. This indicates that even within the same batch, variability in degradation rates must be considered.

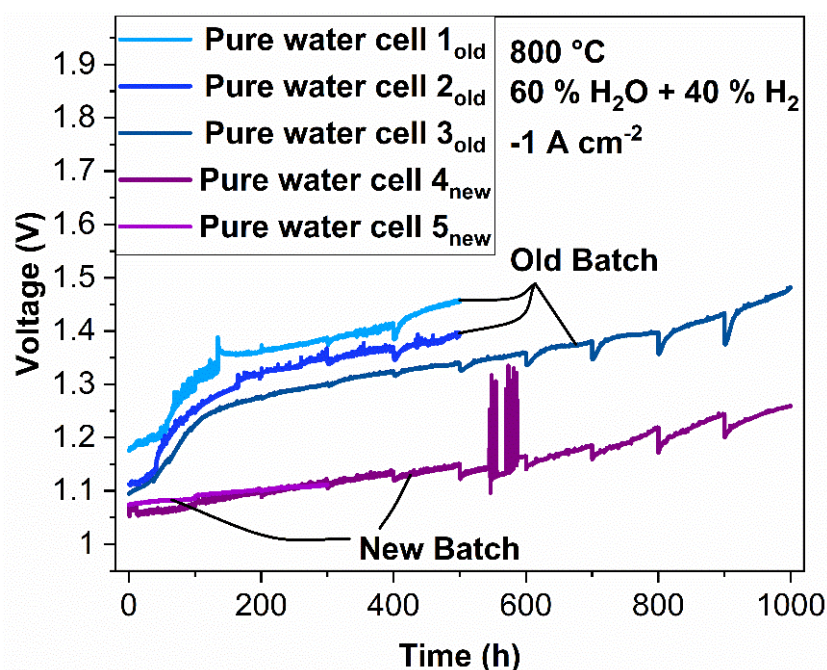


Figure 12 Voltage time plots of individual Ni-YSZ fuel electrode supported cells with steam produced from pure water.

In conclusion, the newer production batch exhibits significantly lower degradation compared to the older batch. This aligns with advancements in manufacturing processes and electrode microstructure optimization, which have improved SOEC durability in recent years ^[19]. Higher initial performance is often associated with lower degradation rates due to reduced electrode

overpotentials ^[119]. In addition, the rapid voltage rise in the first 200 hours observed for pure water cells 1_{old}, 2_{old} and 3_{old} contributes substantially to their overall higher degradation.

Results from similar investigated cells or SOEC systems based on Ni containing fuel electrodes operating in steam electrolysis mode are widely reported in the literature. Many studies document degradation rates below 200 mV·kh⁻¹ ^[26, 120], while larger scale systems have shown even lower degradation rates, often below or around 10 mV·kh⁻¹ ^[24, 121]. Conversely, several publications report significantly higher degradation rates for Ni based fuel electrode supported cells under steam electrolysis conditions ^[30, 88, 115, 122-126]. For instance, degradation rates of 370 mV·kh⁻¹^[31], 600 mV·kh⁻¹^[124] or 880 mV·kh⁻¹^[123] have been reported. In some of these studies, though not all, a rapid voltage increase during the first 200 h of operation was observed, contributing significantly to the high degradation rates ^[30, 88, 115, 122-123]. One major reason is the nickel redistribution through migration, depletion or agglomeration and the accompanied microstructural changes in the fuel electrode ^[31, 115, 123].

In other studies, Si poisoning has been identified as a primary cause of accelerated degradation and was linked to an initial passivation of the SOEC resulting in a sharp rise in operation voltage ^[30, 88, 115]. Additionally, microstructural differences in the fuel electrode have been shown to strongly influence degradation behavior ^[119].

Comparing these studies reveals a broad range of degradation rates for similar Ni-YSZ fuel electrode supported cells and highlights multiple contributing degradation mechanisms. However, as shown in the previous section, cell to cell and batch to batch variability can strongly affect degradation behavior. To better understand the differences between the old and new batch used in this work and to link them to specific degradation phenomena, a more detailed electrochemical investigation and post test characterization are presented in the following sections. For this purpose, two representative cells operated for 1000 h, pure water cell 3_{old} from the old batch and pure water cell 4_{new} from the new batch, were compared. Both cells were tested in the same experimental setup to exclude setup related effects.

Table 3 Degradation rates of the cell operated with steam produced from pure water.

Cell	Operation time (h)	Initial voltage (V)	Degradation rate calculated (mV·kh ⁻¹)	Linear fitting degradation (mV·kh ⁻¹)
Pure water cell 1 _{old}	500	1.176	522	227 (200 - 500 h)
Pure water cell 2 _{old}	500	1.119	564	217 (200 - 500 h)
Pure water cell 3 _{old}	1000	1.101	374	215 (200 - 1000 h)
Pure water cell 4 _{new}	1000	1.062	209	186
Pure water cell 5 _{new}	300	1.074	147	126

6.1.1.2 Current Density Voltage Curves

To investigate the initial voltage increase observed in pure water cells 1_{old}, 2_{old} to 3_{old} but not in pure water cells 4_{new} and 5_{new}, the two cells that operated for more than 1000 hours are compared in more detail. Figure 13 displays the iV curves recorded every 100 hours during the stability tests of pure water cell 3_{old} and pure water cell 4_{new}. The initial iV curves at 0 h are similar for both cells. The bending of the iV curves at high voltages from 1.2 V to 1.4 V seen for both cells is attributed to mass transport limitations. After 100 hours of operation, pure water cell 3_{old} exhibits a lower slope of the iV curve between 1.2 and 1.4 V compared to the region from OCV to 1.2 V. This curve shape persists for the rest of the operation until 1000 hours. Additionally, from 200 hours onward, a clear hysteresis between the forward and backward scans becomes evident and persists throughout the experiment. The forward scan exhibits higher current densities than the backward scan as indicated by the arrows in the plot. These features are not observed in pure water cell 4_{new} until 500 hours of operation when similar curve shapes and hysteresis appear. Similar observations under various operating conditions have been reported in the literature [17, 31, 127-129]. For instance, Dittrich connected the hysteresis to structural changes in the cell in her thesis [17]. However, a definitive identification of hysteresis should be addressed in future work.

Figure 13c and Figure 13d compare the evolution of the area specific resistance (ASR) and the current density at 1.4 V, respectively. Figure 13c shows the ASR values at OCV as a function of the degradation time, calculated from the iV curves. As expected from the voltage evolution discussed in chapter 6.1.1.1, the ASR of pure water cell 3_{old} increases sharply during the first 200 hours. Between 200 and 800 hours, a more gradual increase is observed, followed by a steeper rise after 800 hours. In total, the ASR increases by 430 mΩ·cm² from 145 mΩ·cm² to 575 mΩ·cm² in case of pure water cell 3_{old}. In comparison, pure water cell 4_{new} exhibits a more moderate and linear increase of 95 mΩ·cm² from 119 to 214 mΩ·cm² over the entire 1000 hour period. In conclusion, pure water cell 3_{old} shows a more pronounced degradation behavior, particularly during the early phase. The ASR trend is consistent with the voltage development discussed in Section 6.1.1.

Figure 13d illustrates the current densities at 1.4 V derived from the respective iV curves. Pure water cell 3_{old} shows a strong decline of 1.64 A·cm⁻² from 2.34 A·cm⁻² to 0.70 A·cm⁻² over the measurement period. In contrast, pure water cell 4_{new} exhibits a smaller, steady decline of 0.66 A·cm⁻² from 2.37 A·cm⁻² to 1.71 A·cm⁻². Thus, a higher total decrease is observed in pure water cell 3_{old}. The current density drop is particularly steep within the first 200 hours (approximately 0.85 A·cm⁻²) in the case of pure water cell 3_{old}, mirroring the rapid ASR increase. In pure water cell 4_{new} the current density declines steadily throughout the test. These results agree with the ASR and voltage trends discussed above.

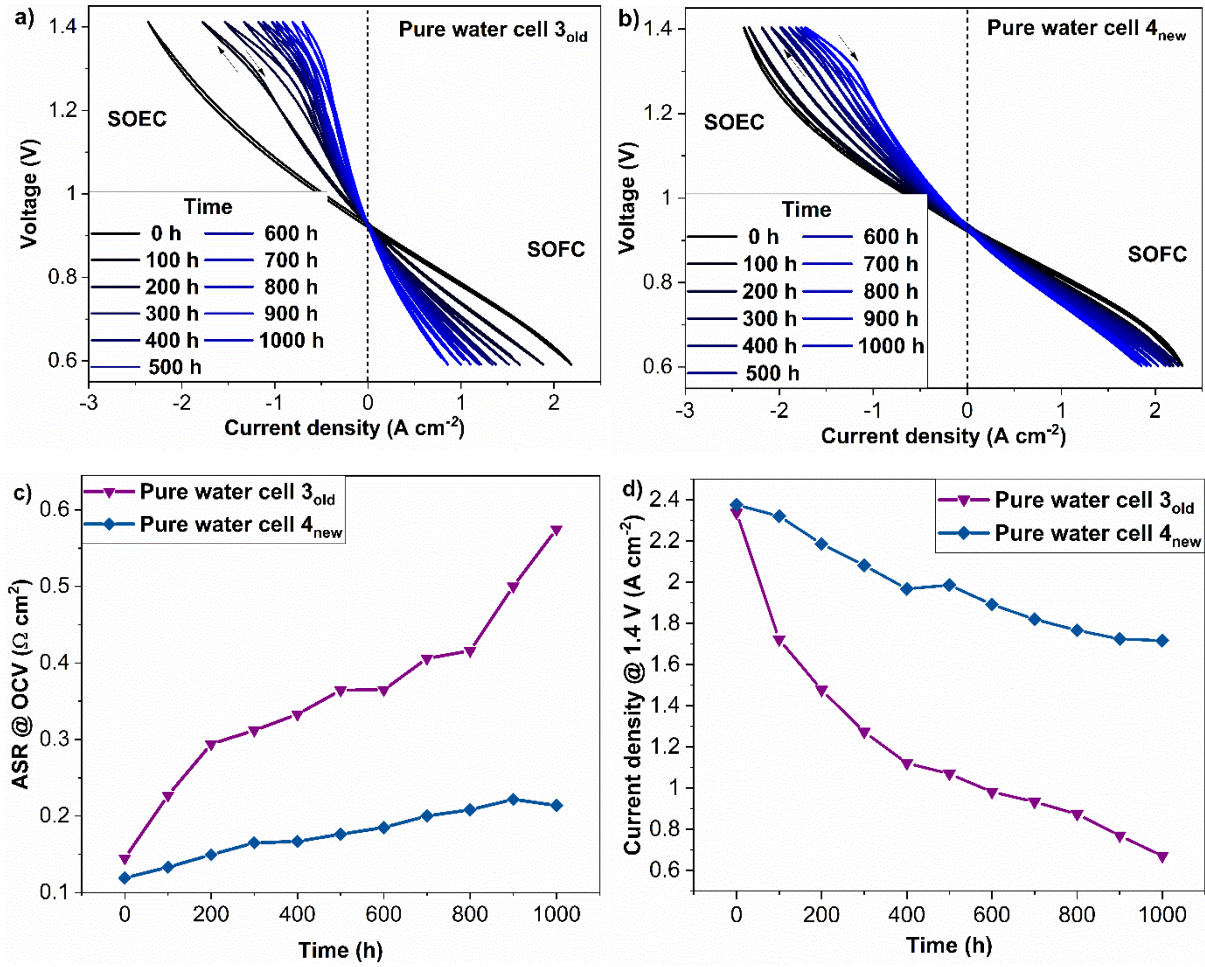


Figure 13 iV characteristics recorded every 100 hours during the stability test for (a) a cell from the old production batch and (b) the new production batch. Comparison of the evolution in (c) ASR values at OCV and (d) the current density at 1.4 V for the old and new production batch.

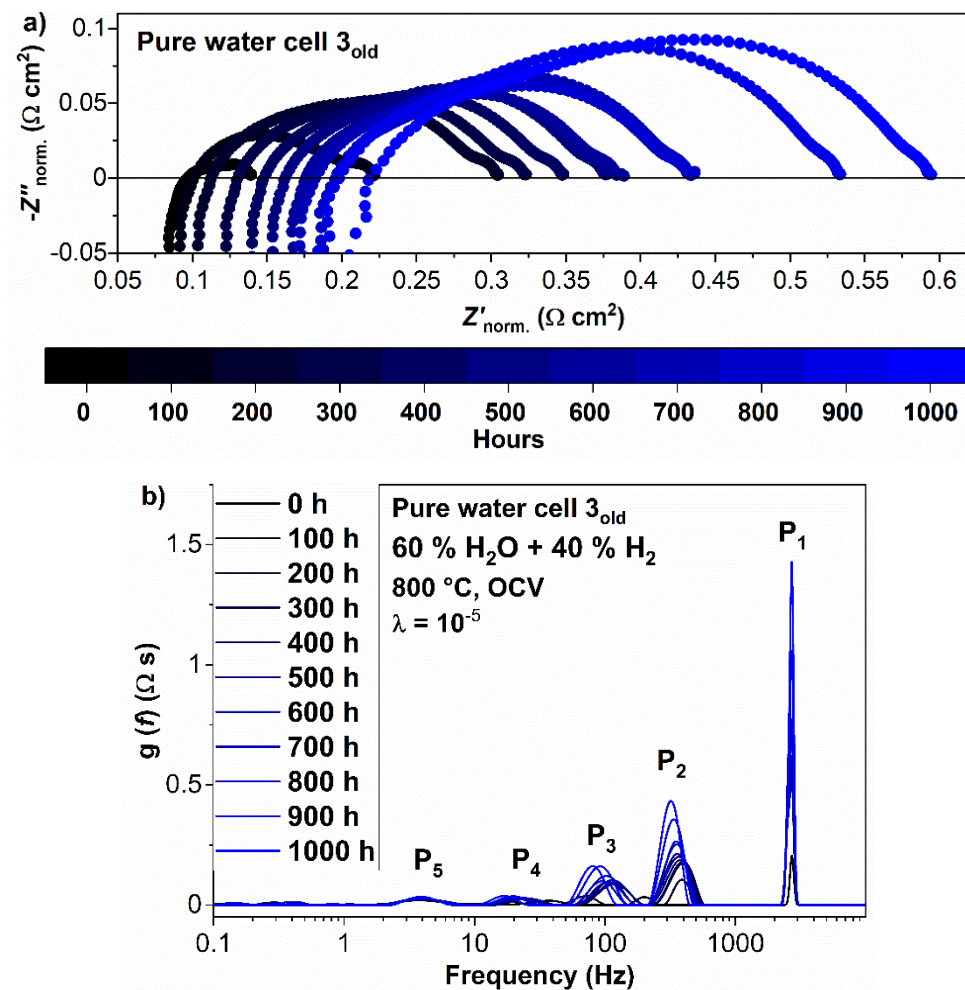
6.1.1.3 Electrochemical Impedance Spectroscopy

The EIS measurements performed at OCV every 100 hours of operation during the stability test are analyzed in this section. The recorded impedance spectra are shown as Nyquist plots for pure water cell 3_{old} and pure water cell 4_{new} in Figure 14a and Figure 14c, respectively. Both cells exhibit an inductive artifact at high frequencies near the intercept with the real x axis. This is attributed to parasitic inductances from the wiring, as commonly reported for the test setup used here and elsewhere [31, 51].

The high frequency intercept with the real axis increases steadily for pure water cell 3_{old} over the operation time. A similar trend is observed for pure water cell 4_{new}, though the increase is less pronounced. However, a direct interpretation of the high frequency ohmic resistance is challenging due to the influence of parasitic inductance and overlap with a high frequency electrochemical process, as described in [51]. The low frequency interception with the real axis increases in both cells, exceeding the high frequency growth. Again, this effect is more pronounced in pure water cell 3_{old} than in pure water cell 4_{new}.

The low frequency region below 10 Hz remains largely unchanged in both cases, whereas the high to intermediate frequency region is most affected. Notably, the increases in both the real and imaginary regions are more significant in pure water cell 3_{old} compared to pure water cell 4_{new}.

At the end of the test, pure water cell 3_{old} exhibits at least three distinguishable semicircles in the Nyquist plot, whereas only two are observed for pure water cell 4_{new}. This indicates that the development of polarization resistance differs between pure water cell 3_{old} and pure water cell 4_{new} and suggests that different processes are responsible for the specific degradation behavior. The corresponding DRT plots (Figure 14b and Figure 14d) confirm that for both cells the processes at low relaxation frequencies between 1 and 100 Hz contribute not significantly to the degradation. The processes referring to the intermediate (300 to 1000 Hz) and the high frequency (3000 Hz) regimes increase in magnitude for both cells; however, this is more significant for pure water cell 3_{old}. In this cell, a particularly rapid increase in magnitudes is observed during the first 200 hours of operation.



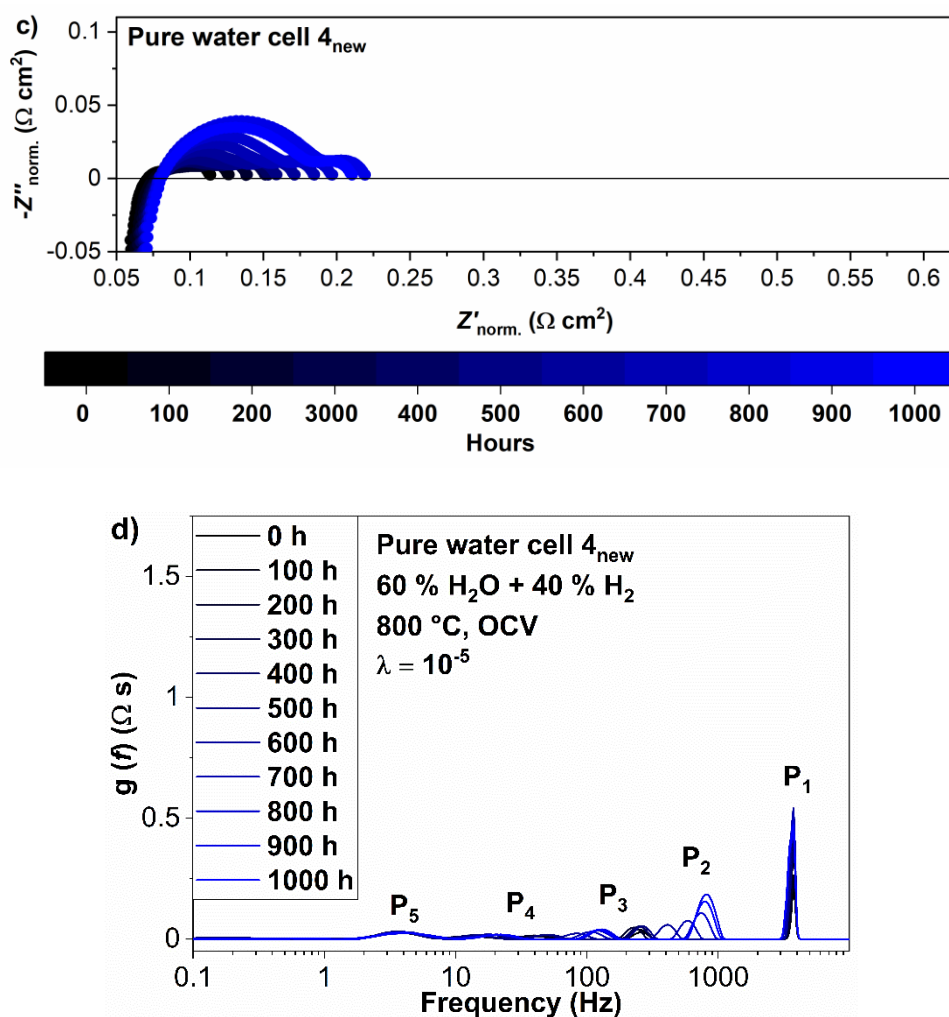


Figure 14 Nyquist plots and DRT spectra derived from EIS data recorded every 100 hours during the stability test for (a, b) a cell from the old production batch and (c, d) the new production batch.

To deconvolute the EIS data and evaluate the ohmic resistance, polarization resistance, and individual electrochemical processes during the stability tests, the data were fitted to an equivalent circuit model (ECM). Based on the DRT plot shown in Figure 15b, corresponding to EIS data recorded at 800 °C and OCV with a gas composition of 60 % H₂O + 40% H₂, an initial estimate of the number of distinguishable time constants was made. A total of five peaks is visible. P_1 as a distinct peak at a relaxation frequency of around 2000 to 3000 Hz, P_2 between 300 to 700 Hz, P_3 at a frequency of 60 to 200 Hz and P_4 and P_5 in the low frequency region with relaxation frequencies between 2 to 10 Hz and 10 to 30 Hz, respectively. However, fitting a model with five separate time constants led to significant fitting errors and decreased manageability. Therefore, a reduced model containing four time constants was chosen, which sufficiently described the system behavior^[17]. Figure 15a shows the Nyquist plot including both the experimental data and the fitted ECM, with the individual RQ elements indicated. The comparison between the DRT of the experimental data and that of the fit demonstrates

excellent agreement as illustrated in Figure 15a. The error (chi square) between the measured data and the fit was in the order of magnitude 10^{-7} .

Furthermore, the absolute and relative residuals (Figure 15c and Figure 15d) exhibit a non sinusoidal profile and remain at low values, indicating a robust fit. The good fit of the simplified four element ECM, despite the presence of five peaks in the DRT, is attributed to the ill posed nature of the DRT inversion problem, which may lead to artificial peak splitting in the intermediate to high frequency region (P_2 to P_4) [58]. Additionally, RQ elements with Q values around 0.8 to 0.9 often lead to additional peaks in the DRT that do not correspond to actual physicochemical processes [58]. In the case of the fitting shown here, this applies to the elements corresponding to RQ_2 and RQ_3 . The ECM configuration discussed is applied consistently for all subsequent cell analyses presented in this thesis.

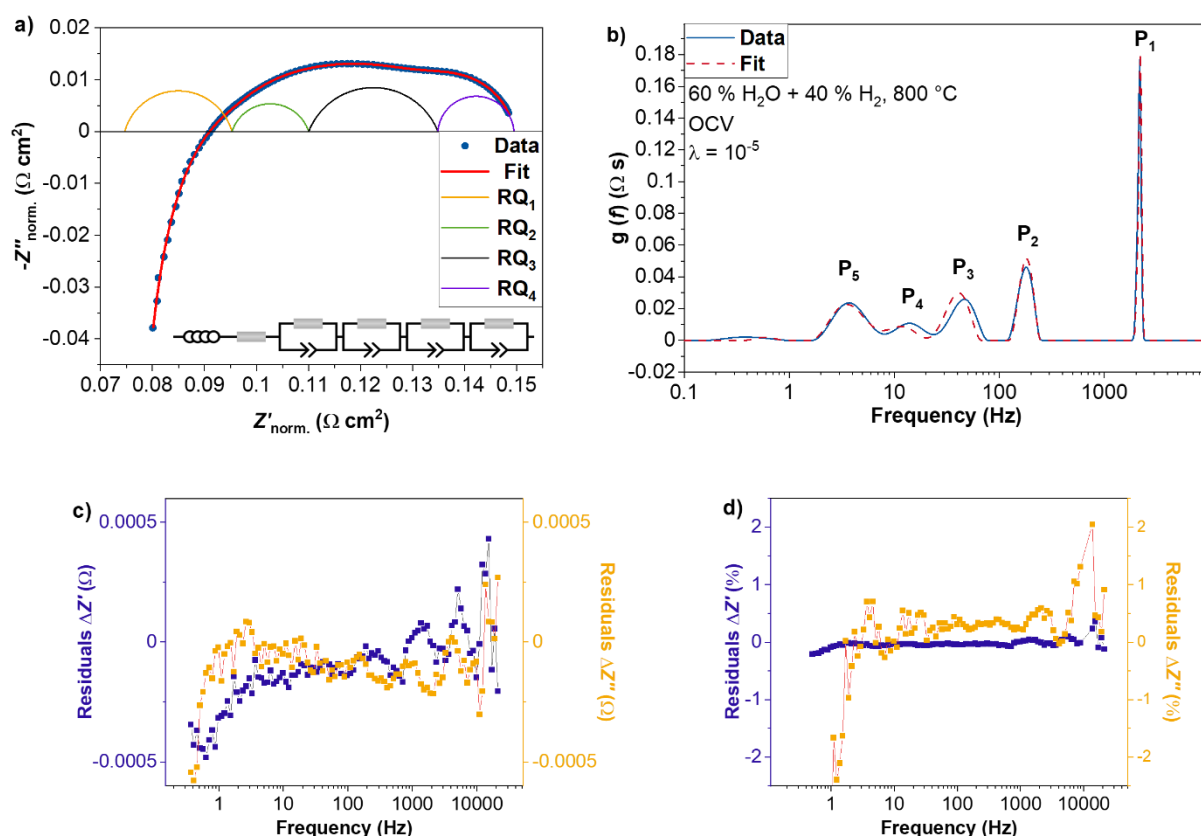


Figure 15 (a) Comparison of Nyquist plot of measured and fitted data, (b) comparison of DRT plots of measured and fitted data with the individual contribution of the 4 RQ ECM model, (c) absolute residuals and (d) relative residuals of the ECM fit in a gas composition of 60 % H_2O + 40 % H_2 at 800 °C and OCV.

The ohmic resistance (R_Ω) and the polarization resistance (R_p) were extracted from the ECM fitting. The evolution of R_Ω as a function of operation time at OCV for pure water cell 3_{old} and pure water cell 4_{new} is shown in Figure 16a. Pure water cell 3_{old} exhibits a higher initial R_Ω of $0.084 \Omega \cdot \text{cm}^2$ in comparison with $0.061 \Omega \cdot \text{cm}^2$ in the case of pure water cell 4_{new}. In the case of pure water cell 3_{old}, R_Ω increases slightly by $0.013 \Omega \cdot \text{cm}^2$ within the first 200 hours, followed by

a more pronounced rise of $0.064 \Omega \cdot \text{cm}^2$ between 200 and 600 hours. In contrast pure water cell 4_{new} does not exhibit a significant increase in R_Ω throughout the entire test duration.

The evolution of R_p at OCV is shown in Figure 16b for both cells. Both cells start with comparable R_p values of $0.061 \Omega \cdot \text{cm}^2$ and $0.057 \Omega \cdot \text{cm}^2$ for pure water cell 3_{old} and pure water cell 4_{new}, respectively. In pure water cell 3, R_p rapidly increases by $0.155 \Omega \cdot \text{cm}^2$ in the first 200 hours. Between 200 and 600 hours, R_p remains constant, before increasing again to a final value of $0.448 \Omega \cdot \text{cm}^2$ by 1000 hours. In contrast, pure water cell 4_{new} shows a continuous, gradual increase in R_p , reaching $0.157 \Omega \cdot \text{cm}^2$ at the end of the test.

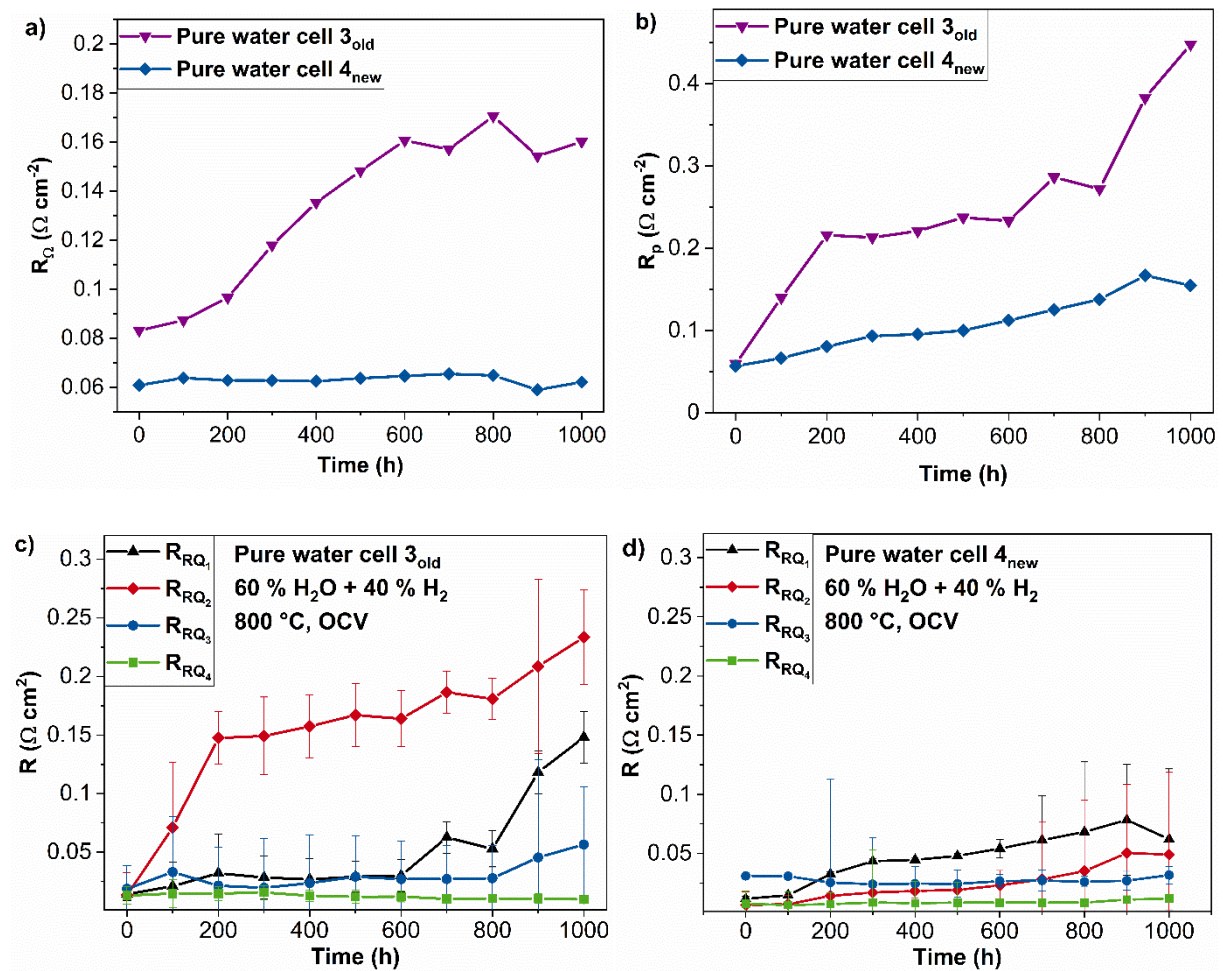


Figure 16 Evolution of the (a) R_Ω , (b) R_p and the individual resistances of the processes (c, d) for a cell from the old production and a cell from the new production batch. All data shown is derived from the ECM fitting of the EIS data recorded every 100 hours during the stability measurement at OCV.

Several conclusions can be drawn from the evolution of both resistances: (1) the lower initial performance of the older cell batch discussed in chapter 6.1.1.1 is mainly due to a higher initial R_Ω compared to the newer cell batch; (2) the dominant contributor to the observed degradation in both cells is the polarization resistance consistent with previous literature reports [31, 124]; (3) the steep voltage rise in pure water cell 3_{old} during the first 200 hours is primarily driven by the

increase in R_p ; (4) the different evolution trends in both R_Ω and R_p suggest that distinct degradation mechanisms are responsible in the two cell batches.

Next, the evolution of the individual processes during operation is compared between the two cells. The resistances of the RQ elements at OCV are plotted as a function of operation time in Figure 16c and Figure 16d for pure water cell 3_{old} and pure water cell 4_{new}, respectively. Minor differences in the initial resistance values are observed between the cells. For instance, the resistance R_{RQ2} exhibits an initial value of $0.006 \Omega \cdot \text{cm}^{-2}$ for pure water cell 3_{old} and a value of $0.012 \Omega \cdot \text{cm}^{-2}$ in the case of pure water cell 4_{new}. These variations are attributed to individual cell characteristics and microstructural differences in the electrodes.

In both cells, R_{RQ1} and R_{RQ2} increase over time, while R_{RQ3} and R_{RQ4} remain approximately constant. The increase in R_{RQ1} and R_{RQ2} is more pronounced for pure water cell 3_{old}.

In pure water cell 3_{old}, R_{RQ2} shows a steep rise within the first 200 hours, while R_{RQ1} increases significantly only after 600 hours. In contrast, in pure water cell 4_{new} both resistances increase gradually and continuously.

From these observations, several conclusions can be drawn: (1) R_{RQ1} and R_{RQ2} are the main drivers for the increase in polarization resistance in both cells whereas R_{RQ4} does not contribute; (2) R_{RQ2} drives the rapid initial degradation in pure water cell 3_{old}, explaining the higher degradation rate of the older batch discussed in chapter 6.1.1.1; (3) the differing resistance evolutions again indicate different degradation mechanisms occurring in both cells. Assigning the RQ elements to electrochemical processes enables further interpretation. The assignment is based on literature as shown in chapter 3.2.3. The low frequency process RQ_4 (2 to 9 Hz) is associated with gas transport in the Ni-YSZ fuel electrode due to its temperature independence and the dependency on a variation in fuel gas composition [62, 118, 130]. In literature, the process RQ_3 is attributed mainly to the air electrode due to its dependency on the oxygen content at the LSC air electrode [62, 130]. The contribution of the air electrode to RQ_3 is identified as an electrochemical process at the TPBs of the LSC/GDC electrode and an oxygen electrode transport process. Previous studies identified the process corresponding to RQ_2 as a process at the Ni/YSZ fuel electrode due to its dependence on the fuel gas content and by many groups assigned to the charge transfer reaction [61, 118, 130-131]. The processes RQ_1 is assigned to the ionic transport or in general, transport phenomena in the Ni-YSZ fuel electrode [61].

Furthermore, it is reported that RQ_1 is a coupled process with RQ_2 associated with the charge transfer at the TPB and the oxide ion transport in the YSZ matrix, respectively [59-60]. In addition, it is commonly done in literature to combine the high frequency processes corresponding to RQ_1 and RQ_2 to the Ni-YSZ fuel electrode polarization [59, 124]. The author notes that some overlap between fuel and air electrode contributions cannot be excluded with this approach. As shown in Figure 17, the main degradation effects are associated with the Ni-YSZ fuel

electrode and the electrochemical reaction. In addition, the electrochemical reaction at the TPB of the Ni-YSZ fuel electrode is responsible for the rapid increase in voltage in the first 200 hours of operation observed in pure water cell 3_{old}. Other authors reported similar degradation behavior identifying a rapid increase in the resistance associated with the TPB reaction in the Ni-YSZ fuel electrode [30, 124, 132].

In summary, the differences in long term stability between the two cells and the two production batches are primarily caused by the differing evolution of processes related to the Ni-YSZ TPB (R_{RQ1} and R_{RQ2}), alongside a moderate contribution from variations in ohmic resistance.

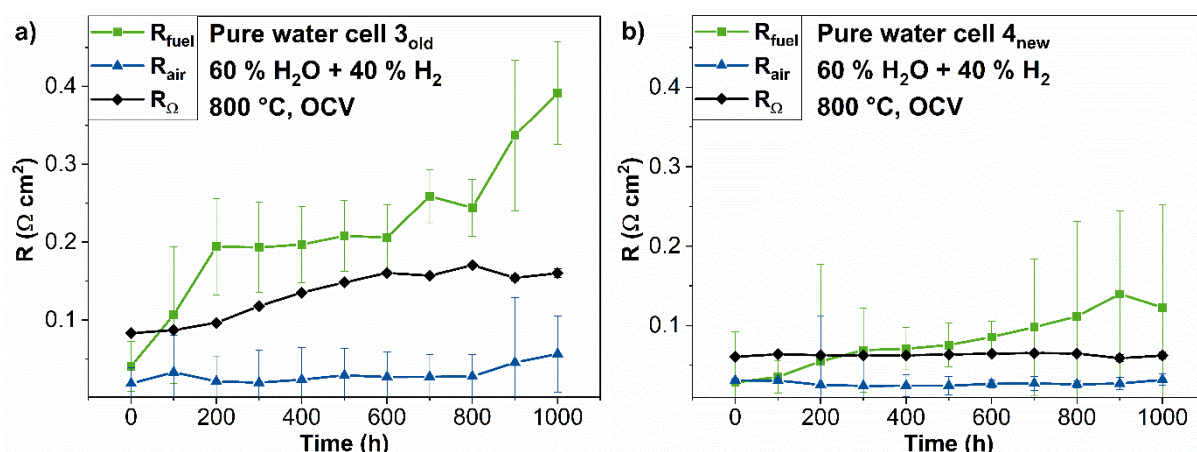


Figure 17 Evolution of the R_{Ω} , the resistance corresponding to the Ni-YSZ fuel electrode and the resistance corresponding to the air electrode for (a) a cell from the old production and (b) a cell from the new production batch.

6.1.2 Post Test Characterization

To gain insights into microstructural evolution, scanning electron microscopy (SEM) images of fractured Ni-YSZ fuel electrode cross sections from a pristine reduced cell, pure water cell 3_{old} and pure water cell 4_{new} are shown in Figure 18. It should be noted that microstructural interpretation must be done cautiously due to the nature of the fractured cross sections, which may introduce artifacts [126]. All samples exhibit good contact between the Ni-YSZ fuel electrode and the YSZ electrolyte. However, small nanoparticles cover some particles in pure water cell 3_{old} which are not present in the case of pure water cell 4_{new} or the pristine reduced cell. Similar nanoparticle features have been reported in the literature for Ni-YSZ fuel electrodes operated under pure water electrolysis conditions [126, 133-134]. In those studies, the nanoparticles were identified as ZrO_2 precipitates formed on the Ni surfaces in the active region of the fuel electrode. Until now it is believed that the formation of these ZrO_2 nanoparticles is related to the reduction of ZrO_2 at the Ni- ZrO_2 interface forming Ni_xZr_y and the reoxidation and reformation of Ni and ZrO_2 depending on the local partial pressure of oxygen [126, 133-134]. Since the local oxygen partial pressure is strongly influenced by the overpotential at the fuel

electrode, regions with higher overpotentials are more susceptible to ZrO_2 nanoparticle formation. This supports the hypothesis that the more severe degradation in pure water cell 3_{old} is associated with locally elevated overpotentials, as also reflected in the electrochemical analysis. A detailed mechanism hypothesis can be found in ^[126].

The preferential appearance of ZrO_2 nanoparticles on Ni grain surfaces suggests possible detachment of Ni-Ni or Ni-YSZ interfaces. Such microstructural changes likely contribute to the observed increase in polarization and ohmic resistances. To validate this further, embedded and polished cross sections will be examined in the next step to eliminate fracture induced artifacts.

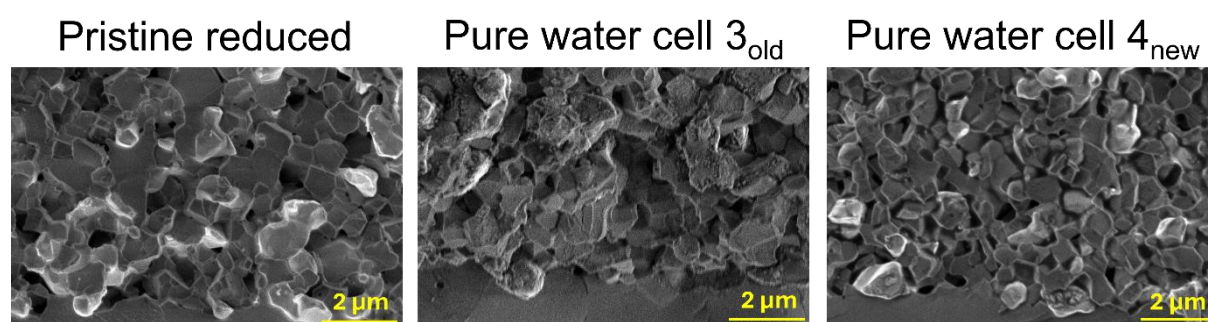


Figure 18 SEM images of the fractured cross section of the electrolyte/Ni-YSZ electrode active area interface for a pristine reduced, pure water cell 3_{old} from the old production batch and pure water cell 4_{new} from the new production batch.

For further analysis, SEM images of the polished cross sections of the Ni-YSZ fuel electrode from a pristine reduced cell, pure water cell 3_{old} and pure water cell 4_{new} are compared in Figure 19a. In these images, the brighter regions correspond to Ni, while the darker areas represent the YSZ phase. In the pristine reduced cell, a well connected Ni-YSZ microstructure is observed throughout the active layer. A similar microstructure is present in pure water cell 4_{new} though a qualitative densification of the active layer can be identified. In the case of pure water cell 3_{old}, this densification appears even more pronounced.

In addition, the red arrows indicate interfacial gaps or phases between the Ni and the YSZ phases. These are present particularly near the electrode/electrolyte interface. These are likely related to the ZrO_2 nanoparticle formation described earlier. Such gaps reduce the triple phase boundary (TPB) length by physically separating the electronically conductive Ni from the ionically conductive YSZ. An increase in ohmic resistance is possible due to the growth of a nonreactive layer near the electrolyte/electrode interface. The observation is consistent with the higher R_Ω values seen in pure water cell 3_{old} compared to pure water cell 4_{new}.

Furthermore, inclusions within the Ni grains, visible as black dots and indicated by the red squares in Figure 19a, were further analyzed by SEM-EDX line scans as shown in Figure 19b. These black inclusions were identified as Si containing impurities incorporated into the nickel

particles. Similar features were previously reported in the literature, where they were assigned to Si oxides particles resulting from impurity incorporation during operation [126]. In literature, a rapid increase in voltage is often associated with the poisoning of the Ni-YSZ fuel electrode by Si impurities in the feed gas or in the cells used [30, 89]. Thus, the rapid increase in voltage and polarization resistance observed for pure water cell 3_{old} is explained by Si poisoning and the blocking of active sites in accordance with the passivation of the Ni sites in the Ni-YSZ fuel electrode [88]. Though, Si incorporation reduces electrochemical activity, leading to increased local overpotentials. These local overpotentials could drive the formation of ZrO₂ nanoparticles at the Ni-YSZ interfaces and explain their occurrence. A detailed mechanism of Si incorporation and its impact on Ni-YSZ degradation is discussed in [33, 135].

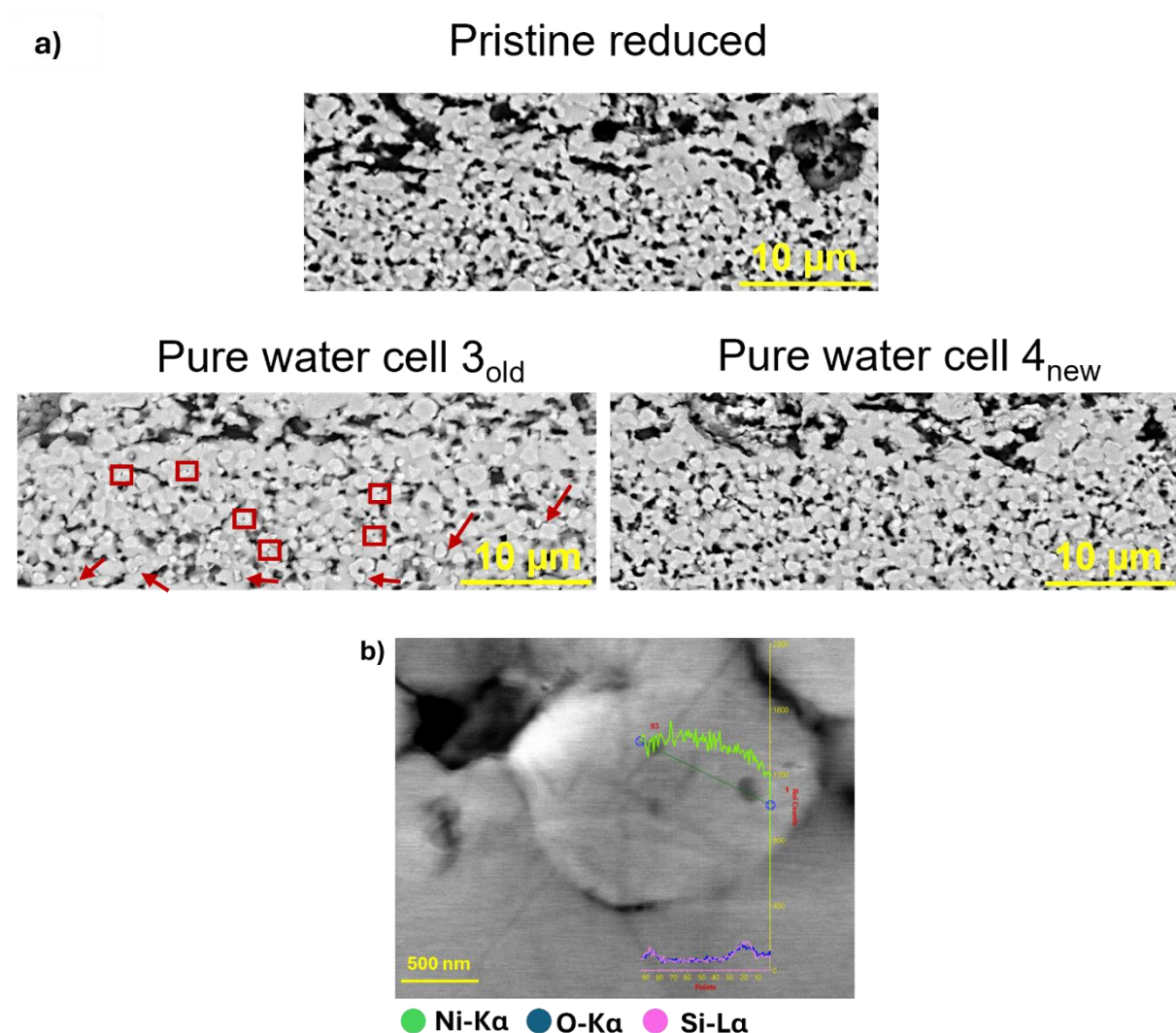


Figure 19 (a) SEM images showing the embedded and polished cross section of the Ni-YSZ electrode active layer of a pristine reduced cell, pure water cell 3_{old} from the old production batch and pure water cell 4_{new} from the new production batch. Red arrows indicate gaps between the Ni and YSZ phases, while red squares mark inclusions within the Ni particles. (b) SEM-EDX analysis of a Ni particle in the Ni-YSZ active layer of pure water cell 3_{old}.

The SEM images and the corresponding EDX maps of the Ni (orange) and YSZ (red) phases for a pristine reduced cell, pure water cell 3_{old} and pure water cell 4_{new} are shown in Figure 20. In all cells, the less porous active functional layer with a thickness of around 10 μm adjacent to the electrolyte is clearly distinguishable from the more porous support structure of the Ni-YSZ fuel electrode.

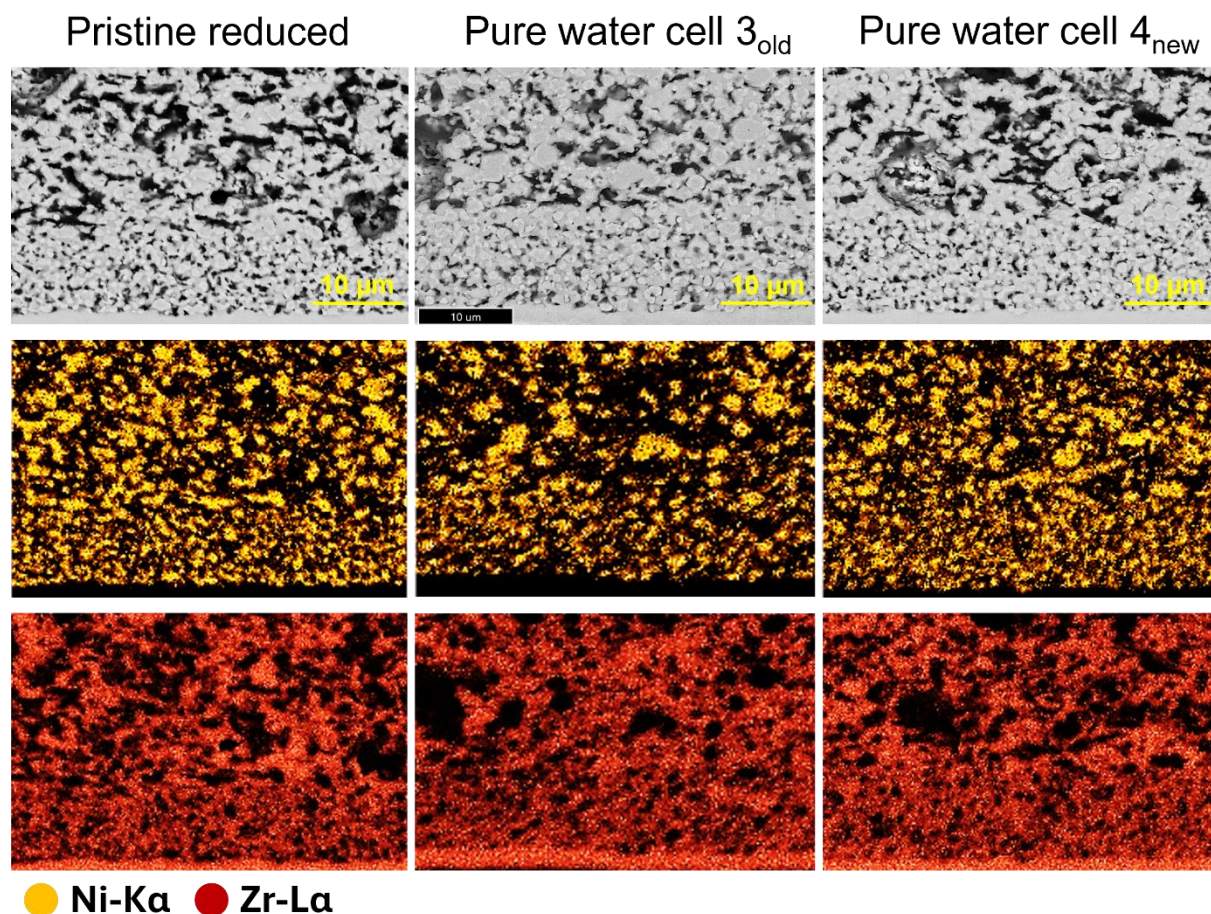


Figure 20 SEM-EDX analysis of the Ni-YSZ fuel electrode of a pristine reduced cell, pure water cell 3_{old} from the old production batch and pure water cell 4_{new} from the new production batch.

Quantitative data derived from the SEM/EDX images, including the Ni and Zr phase fractions, porosity, and particle sizes in the active and support layers, are summarized in Table 4. The Ni phase of the pristine reduced cell appears well distributed and highly interconnected with small, discrete individual Ni particles. In contrast, pure water cell 4_{new} exhibits a slight agglomeration of Ni particles in the active functional layer near the electrolyte compared to the pristine reduced cell. Pure water cell 3_{old} shows a higher Ni agglomeration and a depletion of the Ni fraction in the active layer compared to pure water cell 4_{new}. Both operated cells also exhibit an increased Zr fraction and reduced porosity in the active functional layer relative to the pristine sample. The mean Zr particle diameter increases for both cells compared to the pristine reduced sample. These phenomena result in a densification of the Zr phase that can

be qualitatively seen in the EDX images in Figure 20 . The densification is more pronounced in pure water cell 4_{new}. In summary, the Ni phase is significantly influenced in pure water cell 3_{old} whereas in both cells the Zr phase undergoes microstructural changes which are more pronounced in pure water cell 4_{new}.

Table 4 Quantitative analysis using the SEM/EDX images for the active functional layer and support layer of the Ni-YSZ fuel electrode.

Fraction	Pristine active layer	Pristine support layer	Pure water cell 3 _{old} active layer	Pure water cell 3 _{old} support layer	Pure water cell 4 _{new} active layer	Pure water cell 4 _{new} support layer
Porosity	28 %	39 %	26 %	33 %	22 %	32 %
Ni fraction	30 %	27 %	26 %	23 %	31 %	27 %
Zr fraction	42 %	34 %	46 %	44 %	47 %	41 %
Average						
Ni particle size	0.97 μm	1.09 μm	1.04 μm	1.01 μm	0.99 μm	1.06 μm
Average						
Zr particle size	1.12 μm	1.39 μm	1.23 μm	1.65 μm	1.31 μm	1.42 μm

The agglomeration and depletion of Ni in the functional layer of the Ni-YSZ fuel electrode are known degradation processes in SOECs and directly linked to performance losses ^[29, 31]. The increased operation voltage and polarization resistance observed for pure water cell 3_{old} are consistent with these degradation mechanisms. In addition, the higher degradation in pure water cell 3_{old} compared to pure water cell 4_{new} is explained by the more pronounced Ni agglomeration and depletion. The more pronounced Ni agglomeration in pure water cell 3_{old} is likely exacerbated by the presence of Si impurities identified earlier in the electrode. Such impurities may enhance Ni mobility, promoting migration and agglomeration ^[136]. Furthermore, the blocking TPBs by impurities could lead to higher local overpotentials, accelerating Ni migration ^[89].

Although both cells exhibit decreased porosity in the active functional layer, EIS data (see chapter 6.1.1.3) indicated no significant impact on the gas diffusion resistance. However, both cells show Zr phase densification in the active layer. This phenomenon is not detailed described in literature until now as the microstructural changes in the Ni phase are dominant. In one study an increase in YSZ particles size in the support layer of the Ni-YSZ fuel electrode was reported after operation ^[137]. Another study identified a slight coarsening of the YSZ phase

after SOEC operation ^[138]. In both studies a clear link to the electrochemical degradation of the Ni-YSZ fuel electrode has not been established.

Nevertheless, densification of the Zr phase may reduce the TPB length and the number of electrochemically active sites, which negatively affects the long term stability. Changes in the YSZ microstructure could influence Ni mobility and its microstructural evolution. Thus, further studies are needed to evaluate the role of Zr phase densification in the long term stability degradation and its interaction with Ni related degradation mechanisms.

In conclusion, the differing degradation behaviors seen in both cells are strongly linked to their respective microstructural evolution. The more pronounced increase in ohmic resistance in pure water cell 3_{old} is attributed to the formation of interfacial gaps between the Ni and YSZ phase artificially increasing the electrolyte thickness which is not observed in pure water cell 4_{new}. The accelerated rise in voltage and polarization resistance during the first 200 hours of operation in pure water cell 3_{old} is associated with the Ni-YSZ fuel electrode, in particular the charge transfer process. This is explained by the presence of Si poisoning, increased Ni depletion and agglomeration, and the formation of ZrO₂ nanoparticles which are not seen in pure water cell 4_{new}. Since both investigated cells were operated in the same test setup, the differences are attributed to batch specific factors. It is believed that the Si poisoning observed is due to impurities in the cells' materials which was reported before in literature as a suggestion ^[33, 89].

Based on these findings, in the next chapters only cells from the same cell production batch are compared regarding stability tests to ensure comparability. While minor differences in the initial performance (within 10 to 70 mV) and degradation rates must be still considered, the evolution of the operation voltage was consistent within each cell batch which allows a meaningful comparison of degradation behavior.

6.2 Direct Utilization of Seawater

Steam electrolysis was investigated using steam generated directly from seawater to evaluate its applicability in SOECs for hydrogen production. Initially, the performance of SOECs operated with seawater derived steam is evaluated at various operation parameters. Afterwards, the initial performance of seawater operation was compared with single cells operating with steam from ultrapure water. The production batch of each tested cell is indicated by a subscript. The short term degradation behavior of seawater operated single cells from the old production batch was studied at different temperatures and steam contents. The stability of the SOECs operated with seawater was evaluated and compared to a cell operated with ultrapure water from the new production batch (pure water cell 4_{new}, see chapter 6.1). Post test characterization of the degraded cells was conducted to analyze salt deposition and the influence of seawater utilization. All experiments were carried out on commercial

state-of-the-art single cells supplied by Elcogen, featuring optimized electrode microstructures and cell designs. Some of the iV curves and EIS measurements for the evolution of the initial performance and the short term degradation measurements of the seawater operation were conducted in collaboration with Bintou Issa Dembele during her master thesis in the WASCAL exchange program ^[139]. SEM-EDX analysis of the polished Ni-YSZ fuel electrode cross sections was performed in cooperation with Jean Pierre Puc and Pritam Chakraborty from the working group of Dr. Basak at IET-1 Forschungszentrum Jülich.

6.2.1 Electrochemical Initial Performance

This section evaluates the electrochemical initial performance of state-of-the-art Ni-YSZ fuel electrode supported single cells using steam generated directly from seawater. Firstly, iV curves recorded at varying temperatures and steam content are presented and analyzed. After that, the performance based on iV curve measurements under identical conditions is compared to baseline experiments using steam derived from ultrapure water. Finally, the activation energies of the area specific resistance (ASR) values are calculated for both seawater and ultrapure water operated cells to enable an evaluation of their temperature dependent behavior.

6.2.1.1 Temperature Dependency

The performance of steam electrolysis using directly evaporated seawater was investigated under varying operating conditions. Figure 21 shows the iV curves of different individual cells recorded under a variation of the operating temperature with a constant gas composition of 60 % H₂O + 40 % H₂. Operation in fuel cell operation mode leads to positive current density values due to power generation, whereas negative current densities are related to electrolysis operation and power consumption. As predicted by the Nernst equation, the open circuit voltage (OCV) increases with decreasing operation temperature. The theoretically calculated OCV by the Nernst equation and the experimental observed OCVs for the measured cells are shown in Table A 10 in the appendix. The experimentally determined OCVs differ up to 1 % from the theoretically calculated values. Deviations from the OCV are attributed to minor gas leakages between the air and fuel electrode sides ^[90].

For Cell A_{old} the measurement range was chosen between 0.6 and 1.5 V, following previous studies from the working group ^[66-67, 140]. The highest operation temperature of 900 °C exhibits the maximum current density of $-2.03 \text{ A} \cdot \text{cm}^{-2}$. The iV curves recorded at 900 and 875 °C show an initial linear region up to approximately $-1 \text{ A} \cdot \text{cm}^{-2}$ followed by a steeper slope until the maximum current density at 1.5 V is reached in SOEC mode. Below an operating temperature of 875 °C, this behavior changes; the slope decreases after the linear range. This behavior is not seen in Cell B_{old} and Cell C_{new} which were measured in a voltage range of 0.6 and 1.4 V. It is therefore likely that the higher maximum voltage of 1.5 V used for Cell A_{old} caused

microstructural changes and accelerated degradation [141]. As electrode overpotentials are elevated at 1.5 V, this may lead to irreversible damage [142]. Hence, in the subsequent experiments, the maximum voltage during the iV curve measurements is restricted to 1.4 V and detailed electrochemical analysis is only shown for Cell B_{old} and Cell C_{new}.

Cell C_{new} achieved the highest current density in SOEC mode with $-2.90 \text{ A}\cdot\text{cm}^{-2}$ at 1.4 V and 900 °C whereas Cell B_{old} reached a current density of $-2.16 \text{ A}\cdot\text{cm}^{-2}$. These differences are consistent with prior results (chapter 6.1), showing that the newer production batch (Cell C_{new}) exhibits higher initial performances compared to the older batch (Cell B_{old}) due to lower ohmic resistances. In both cells the current density decreases with a decrease in temperature. This is expected as higher temperatures enhance reaction kinetics and increase the conductivities of the electrolyte, the LSC air electrode, the GDC barrier layer and the ionic conductive phase of the Ni-YSZ fuel electrode [143-146].

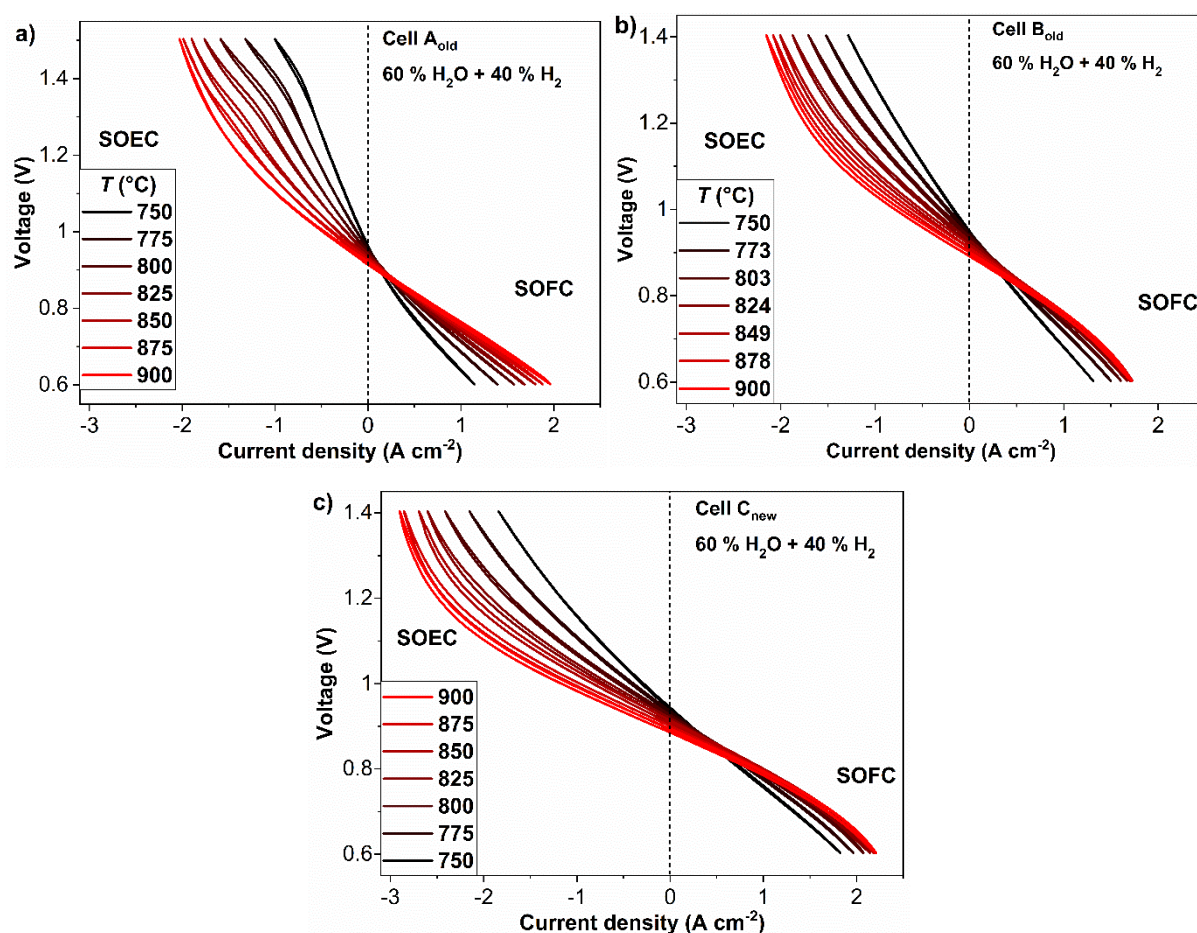


Figure 21 iV curves of three individual (A, B, C) Ni-YSZ fuel electrode supported cells operated with steam produced from seawater at different operating temperatures in a gas composition of 60 % H₂O + 40 % H₂.

In the case of Cell B_{old} and Cell C_{new} at increased temperatures and high current densities, a non linearity and an upward bending of the iV curves are observed. This indicates an influence

of an activation or concentration overpotential. In previous work, this was mostly connected to mass transport limitations as the diffusion overpotential becomes more significant close to the limiting current density caused by a depletion of educt ^[141]. However, the calculated theoretical conversion of steam reaches a maximum of 18 % for the highest measured current density, suggesting that the observed non linearity is likely due to local diffusion limitations within the electrodes, rather than bulk reactant depletion. For operation temperatures above 800 °C a hysteresis in the iV curves is observed. The origin of this hysteresis at elevated temperatures remains under discussion in the literature and has also been reported for steam generated from ultrapure water ^[17].

In summary, SOEC operation with steam produced from seawater is feasible across a range of temperatures. The highest performance is achieved for the highest operation temperature of 900 °C. However, high temperatures pose challenges concerning other SOEC system components. For instance, some state-of-the-art interconnects consisting of LaCrO₃ are limited to an operating temperature of ≤ 800 °C ^[147]. Thus, industrial applications of SOECs are mostly reported between 600 and 850 °C ^[64, 148].

6.2.1.2 Steam Content Dependency

The performance of steam electrolysis using steam directly generated from seawater was evaluated at varying steam contents while maintaining a constant temperature of 800 °C with H₂ as balance gas. iV curves were recorded in a voltage range from 0.6 to 1.4 V. The resulting iV characteristics of two individual cells referred to as Cell D_{new} and Cell E_{new} are presented in Figure 22. The corresponding theoretical and experimentally measured OCV values are provided in Table A 11 in the appendix. As observed previously, the experimental OCV values deviate by up to 1 % from the Nernst equation predictions, which can be attributed to minor gas leakage between the fuel and air sides ^[90].

The highest current densities in SOEC mode were recorded at the highest steam content of 60 % reaching -2.30 A·cm⁻² and -2.19 A·cm⁻² for Cell D_{new} and Cell E_{new}, respectively. Both cells show the same trend that lower steam content results in lower performance of the cells. In addition, both show comparable performance, which is expected due to the same production batch. Minor deviations in current densities between both cells are attributed to the individual cell variability and differences in contacting quality.

For both cells, a steepening of the iV curve slope is observed at high current densities in SOEC mode, which becomes more pronounced as the steam content decreases. For instance, at a steam content of 10 % the iV curves exhibit a nearly vertical slope after surpassing a voltage of approximately 1.2 V in SOEC mode indicating strong transport limitations. The theoretical steam utilization is calculated to be at a maximum of 20 % for both cells. These observations suggest that the performance is increasingly limited by gas phase diffusion at the fuel electrode under lower steam concentrations. By increasing the steam content, the mass transport of

steam to the active site at the electrode is accelerated and thus these limitations are seen at higher current densities. In summary lower steam content results in reduced electrochemical performance, whereas higher steam content improves cell operation. Thus, in the next section a steam content of 60 % is chosen for further evaluations and measurements.

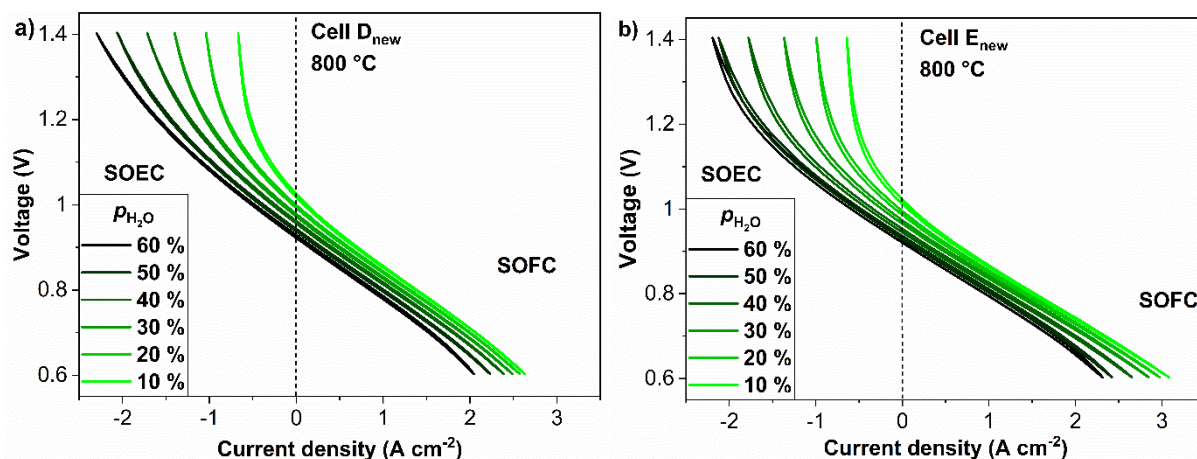


Figure 22 iV curves of two individual (Cell D_{new} and Cell E_{new}) Ni-YSZ fuel electrode supported cells operated with steam produced from seawater at different steam contents with H₂ as balance gas at a constant temperature of 800 °C.

6.2.1.3 Comparison with Pure Water Operation

In the previous section, iV curves for the direct utilization of seawater in SOEC single cells were presented. This raises the question of whether the use of seawater leads to a performance decrease compared to the conventional use of pure water for steam generation. The term pure water is used within the next chapters for ultrapure deionized water. This section compares the iV curves and key performance parameters of cells operated with steam derived from seawater and pure water.

Based on the iV curves in the previous chapters, key performance parameters such as the current density at 1.4 V or the ASR at OCV are used to analyze the impact of seawater utilization on the initial performance. Figure 23a compares representative iV curves of a pure water and a seawater operated cell from the new production batch under identical conditions. Both measurements are conducted in the same experimental setup and with a gas composition of 60 % H₂O + 40 % H₂ at 800 °C. Both cells exhibit similar current density values and iV curve shapes. At 1.4 V current densities of $-2.34 \text{ A} \cdot \text{cm}^{-2}$ and $-2.21 \text{ A} \cdot \text{cm}^{-2}$ were measured for the cells operated with pure water and the cell operated with seawater, respectively.

Figure 23b and Figure 23c present the current densities at 1.4 V as function of operation temperature and steam content for several cells operated with either seawater or pure water. In the case of temperature variation, the highest and lowest current densities were both observed for cells operated with seawater. This variability is attributed to differences between

the new and old production batches, as discussed in chapter 6.1. The pure water cells fluctuate in current density values as well. For example, the highest current density at 1.4 V and 900 °C achieved for a pure water operated cell is $-2.63 \text{ A}\cdot\text{cm}^{-2}$ whereas the lowest value is $-2.26 \text{ A}\cdot\text{cm}^{-2}$. These cells originate from the older production batch, and the variations are likely caused by differences in cell contacting.

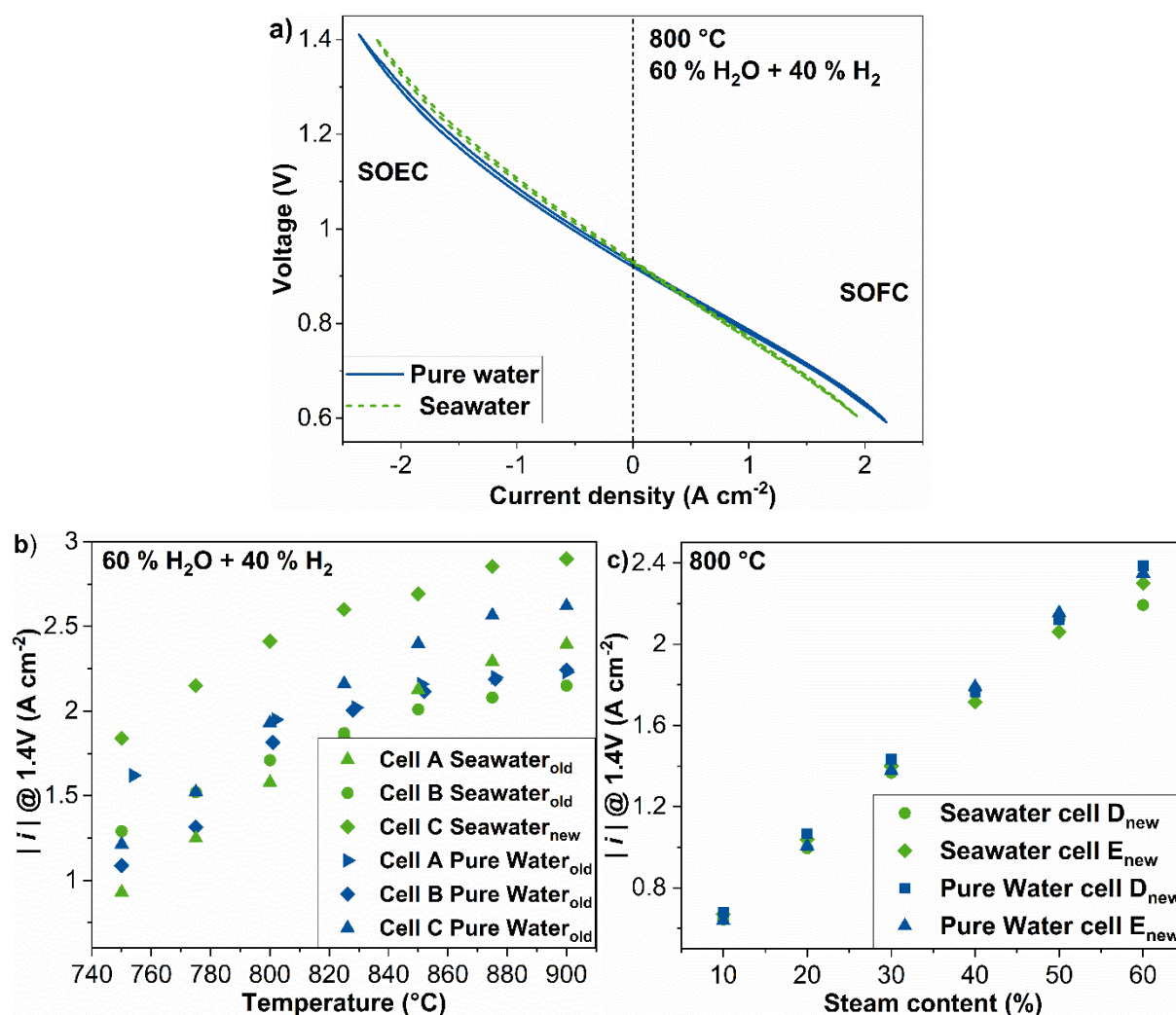


Figure 23 Comparison of individual Ni-YSZ fuel electrode supported cells operated with steam produced from seawater and pure water as (a) iV curves at 800 °C in 60 % H₂O + 40 % H₂, (b) current densities at 1.4 V in 60 % H₂O + 40 % H₂ at different operating temperatures and (c) current densities at 1.4 V and 800 °C for different steam contents with H₂ as balance gas.

The two seawater operated cells from the old production batch show similar performance comparable to their pure water counterparts, indicating no influence on the performance from seawater use at varying temperatures. Regarding different steam contents, the current densities do not fluctuate as much, and similar performances were observed when comparing pure water and seawater measurements. Here, seawater and pure water operation exhibit nearly identical results. In general, the results suggest that steam electrolysis using seawater

does not significantly affect current density. Performance variations are primarily attributed to cell to cell variability, contacting and production batch differences, rather than the water source. Another key performance parameter in steam electrolysis is the area specific resistance (ASR) of the cells. From the recorded iV curves, the ASR values are calculated from the slope. Based on the recorded iV curves, ASR values were derived from the slope of the voltage–current relationship. Activation energies were subsequently calculated using the Arrhenius equation. Figure 24 displays the respective Arrhenius plots of two cells operated with steam produced from seawater (Seawater Cell B_{old} and Seawater Cell C_{new}). The ASR values were determined at OCV and a current density of $-0.5 \text{ A}\cdot\text{cm}^{-2}$ in electrolysis mode. A first analysis follows the conventional approach of linear Arrhenius fitting which is widely applied in literature as shown in Figure 24a and Figure 24b [51, 66-67, 140]. Two temperature regimes are distinguished in the Arrhenius plots of both cells. The first temperature regime ranges from 750 to 825 °C with steeper slope indicating higher activation energies. The second temperature regime ranges from 850 to 900 °C where the slope flattens corresponding to lower activation energies. A similar trend was found in CO₂ electrolysis conditions by previous work of our working group on the same cell types which reported a transition around 832 °C between linear ASR dependence and a temperature independent regime [17]. Furthermore, a similar trend of slope flattening at higher temperatures is reported for SOECs with other fuel electrodes than Ni-YSZ [149].

To account for this, a model comprising both a thermally activated electrochemical contribution and a temperature independent gas transport resistance is applied [61-62, 150-151]. By fitting the ASR data into a model that consists of a thermally activated electrochemical contribution and a temperature independent contribution from the gas concentration (diffusion and/or conversion) the flattening of the ASR is treated. This approach corresponds to equation 6.1 where R_{diff} corresponds to the constant gas diffusion and conversion resistance and R_0 to the pre exponential factor [149]. Following this approach, the respective fitting of the ASR is shown in Figure 24c and Figure 24d for both seawater operated cells. The fitted gas concentration related constant resistance is in the order of 0.07 to 0.1 $\Omega\cdot\text{cm}^2$ at OCV corresponding to fuel and air electrode gas concentration processes. These values are in the order of reported literature values for fuel electrode support structure with pores under 1 μm [152]. Here, the values depend strongly on the measurement geometry and the used gas atmosphere. Differences in the value between individual cells hint at different microstructures related to porosities and tortuosity of the electrode structures and differences in the binary gas diffusion within the current collectors or stagnant gas layers in the setups [152-153]. At a current density of $-0.5 \text{ A}\cdot\text{cm}^{-2}$ the calculated R_{diff} are in the order of 0.06 to 0.09 $\Omega\cdot\text{cm}^2$ and thus slightly lower compared to the values at OCV. This is in line with reported trends of decreasing transport resistance at increasing current densities [153-155]. In electrolysis mode, the gas composition in

the active layer of the electrodes changes due to the conversion of the reactant. For instance, at the Ni-YSZ fuel electrode the gas conversion resistance is theoretically the lowest when the molar ratio of reactant and products is one [48]. Thus, in electrolysis mode the steam content of the initial gas compositions of 60 % H₂O + 40 % H₂ is decreased and the molar ratio of H₂O to H₂ is pushed towards 1. Furthermore, the Knudsen diffusion coefficient of H₂O is smaller compared to H₂ due to its higher molecular weight. Thus, a decrease in gas diffusion resistance could be explained by the higher molar ratio of H₂ at the active layer of the Ni-YSZ fuel electrode reducing the Knudsen diffusion in the porous electrode.

$$ASR = R_0 e^{\left(\frac{E_a}{kT}\right)} + R_{diff}. \quad (6.1)$$

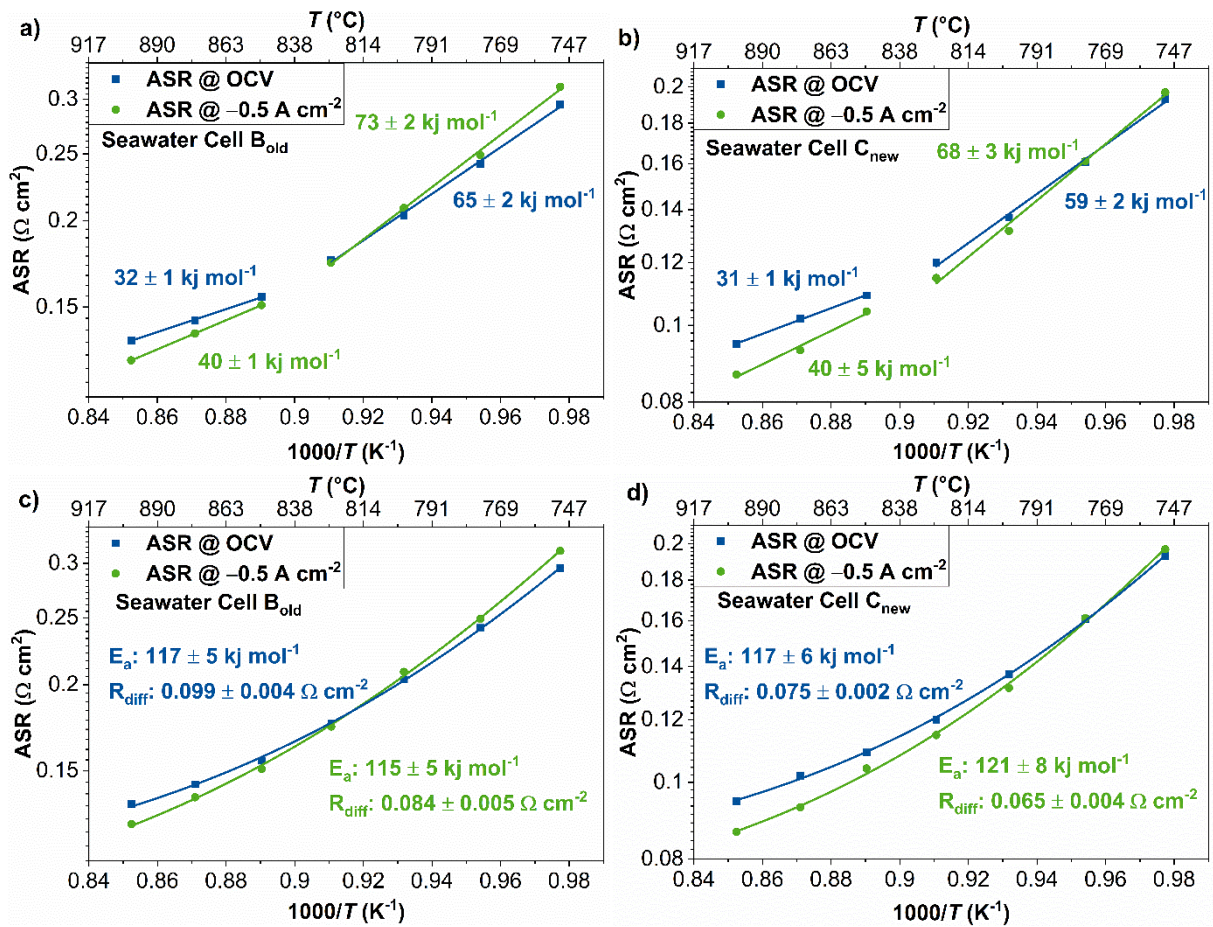


Figure 24 Arrhenius plots of two seawater operated cells with (a), (b) a separate linear fit for the calculation of two activation energies for the temperature ranges 750 to 825 °C and 850 to 900 °C and (c), (d) fitting the data to a model taking account a constant gas concentration contribution to calculate the activation energy at OCV and an electrolysis current of -0.5 A·cm⁻².

The activation energy of the ASR was also evaluated for cells operating with steam generated from ultrapure water. The resulting values for R_{diff} and the activation energies are shown in Table 5. Similar activation energies at OCV reaching from 103 to 156 kJ·mol⁻¹ and at

$-0.5 \text{ A}\cdot\text{cm}^{-2}$ reaching from 118 to $154 \text{ kJ}\cdot\text{mol}^{-1}$ are calculated for the pure water cell compared to the seawater operated cells. Furthermore, similar values for the gas transport resistance are observed, reaching from 0.078 to $0.1152 \text{ }\Omega\cdot\text{cm}^2$ at OCV and from 0.071 to $1.100 \text{ }\Omega\cdot\text{cm}^2$ at $-0.5 \text{ A}\cdot\text{cm}^{-2}$. These values are within the expected experimental variation and show no significant deviation between seawater and pure water operation regarding transport related limitations or the thermal activation of electrochemical processes. In conclusion, the use of seawater in SOECs does not negatively influence the initial performance compared to conventional operation with ultrapure water. These results on real seawater utilization are in accordance with literature studies on the direct use of seawater in SOEC single cells [9, 14-15].

Table 5 Calculated activation energies and the gas concentration resistance from a model taking into account a constant gas concentration contribution in the temperature range from 750 to $900 \text{ }^\circ\text{C}$ for two cells operated with steam from seawater and three cells operated in pure water conditions at OCV and $-0.5 \text{ A}\cdot\text{cm}^{-2}$ electrolysis current.

Cell	E_a @ OCV ($\text{kJ}\cdot\text{mol}^{-1}$)	E_a @ $-0.5 \text{ A}\cdot\text{cm}^{-2}$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$R_{\text{diff.}}$ @ OCV ($\Omega\cdot\text{cm}^2$)	$R_{\text{diff.}}$ @ $-0.5 \text{ A}\cdot\text{cm}^{-2}$ ($\Omega\cdot\text{cm}^2$)
Seawater Cell B_{old}	117 ± 5	115 ± 5	0.099 ± 0.004	0.084 ± 0.005
Seawater Cell C_{new}	117 ± 6	121 ± 8	0.075 ± 0.002	0.065 ± 0.004
Pure water Cell A_{old}	116 ± 3	132 ± 11	0.084 ± 0.005	0.084 ± 0.005
Pure water Cell B_{old}	156 ± 18	154 ± 32	0.1152 ± 0.010	0.1100 ± 0.019
Pure water Cell C_{old}	103 ± 9	118 ± 7	0.078 ± 0.009	0.071 ± 0.010

6.2.2 Stability Evaluation

This section investigates the longevity and stability of SOECs operated with steam directly produced from seawater. Evaluating the SOEC stability of seawater utilization is critical due to the potential transport of impurities such as salt aerosols, organic compounds, or trace elements into the electrochemical cell, which may impact performance and durability.

The analysis begins with short term stability measurements (up to 300 hours) with cells from the old production batch with the focus on the influence of varying operating temperatures and steam contents at the fuel electrode. After that, a long term stability measurement of 1000 hours on a cell from the new production batch is conducted and compared to a pure water test to identify the effects of seawater usage. The stability evaluation includes the comparison of iV curves and detailed electrochemical impedance spectroscopy (EIS) to

assess the evolution of ohmic and polarization resistances and identify performance limiting processes. The degraded cells are post test characterized by various techniques to detect and assess the impact of possible impurity transport and to identify degradation mechanisms specific to seawater operation. The surface of the Ni-YSZ fuel electrode was scanned for impurities using XRD, GI-XRD, XPS, and SEM-EDX measurements. Furthermore, the cross sections of the Ni-YSZ fuel electrode are characterized using SEM-EDX to analyze degradation phenomena and correlate them with electrochemical results.

6.2.2.1 Short Term Stability Tests

The degradation behavior during the utilization of seawater was investigated in short term degradation measurements (< 300 hours) under varying operating conditions. The tested cells originated from the old production batch, and a higher degradation rate is expected due to Si poisoning as described in chapter 6.1.

First, the impact of operating temperature was evaluated at 750, 800, and 850 °C. The degradation experiments were performed at a constant voltage of 1.25 V and the temperature was adjusted every 24 hours. During each period, the current response was recorded, and EIS measurements at OCV were performed between temperature changes.

Figure 25a shows the evolution of the current density over time. The current density is generally lower at lower operating temperatures due to reduced O^{2-} ion conductivity of the electrolyte and the electrodes and slower reaction kinetics. The absolute degradation rates for the 24 hours operation periods reach from 48 to 194 mA·cm⁻²/24h, equivalent to up to 8 A·cm⁻²·kh⁻¹. Relative degradation rates vary between 2.9 to 19.1%/24h. These high degradation rates are attributed to the high current densities achieved at 1.25 V reaching over 2.2 A·cm⁻² and the corresponding high electrode overpotentials [115, 120, 123, 156]. For comparison, degradation rates of 6.6 A·cm⁻²·kh⁻¹ were previously reported for similar cells operated at a constant voltage of 1.29 V at 800 °C in pure water conditions at similar or lower resulting current densities [157]. Furthermore, several studies have reported accelerated degradation during the first 100 to 300 hours of SOEC operation, which supports the high initial degradation seen here [30-31, 123, 157].

Regardless of the operating temperatures, the lowest degradation rates at each temperature were observed within the first 72 hours of testing consistent with findings from a previous study using the same cell type [31]. Among the operating temperatures, the highest temperature of 850 °C leads to the lowest relative degradation rates on average. The highest relative degradation rates are obtained from the lowest operating temperature of 750 °C. These results are in accordance with literature studies on SOECs operated with pure water [156, 158]. Other studies reported the reversed effect, a higher degradation rate for an increased operating temperature in pure water conditions [31, 157]. Thus, literature results can be contradictory due

to varying cell designs, operating conditions (galvanostatic or potentiostatic) and developed overpotentials ^[158].

Figure 25b presents the corresponding evolution of the ohmic, and polarization resistance derived from the EIS data. As expected, higher temperatures lead to lower values of ohmic and polarization resistance. It can be rationalized that R_{Ω} stays at constant values between the degradation periods while R_p increases between the degradation periods for all investigated operating temperatures. The average increase in R_p is most pronounced for the lowest operating temperatures. The average increase in R_p is most pronounced for the lowest operating temperature of 750 °C. Furthermore, the highest total and relative increase in R_p is at the lowest operating temperature of 750 °C in accordance with the highest degradation rates. R_p exhibits the lowest total and relative increase in R_p at an operating temperature of 850 °C.

From the observations, it is concluded that an increase in R_p is the primary contributor to performance degradation at all investigated temperatures. In contrast, R_{Ω} does not significantly contribute to the cell's resistance. This is following previous results by our workgroup for pure water measurements on similarly designed single cells ^[31]. Consequently, an operating temperature between 800 and 850 °C appears optimal for seawater based SOEC operation. However, it must be noted that these results were obtained using cells from the old production batch, which were influenced by Si impurities and the corresponding degradation. This may influence the observed temperature dependence of degradation behavior and should be considered.

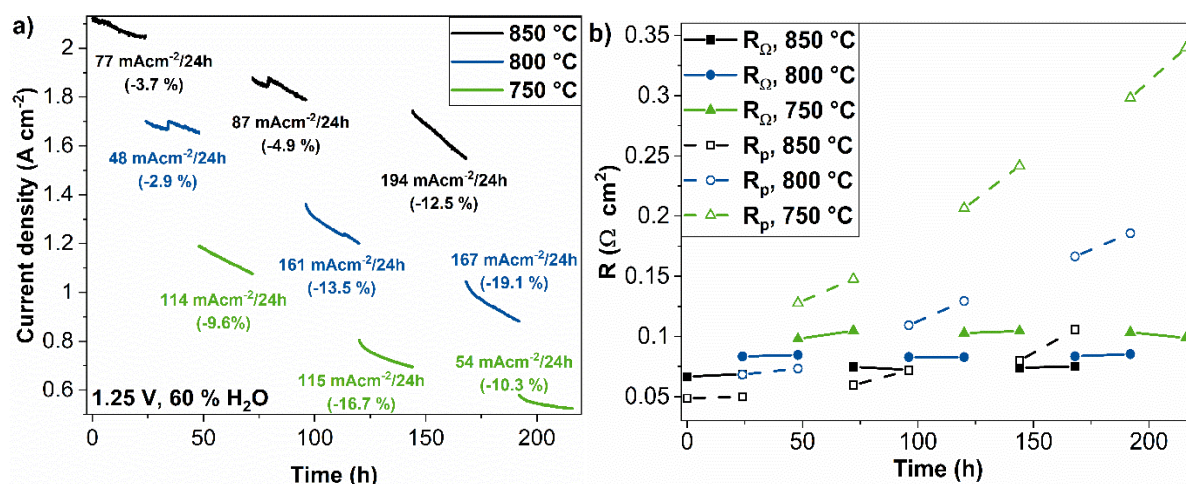


Figure 25 (a) Short time current density against time curves at 850 °C, 800 °C and 750 °C at a constant voltage of 1.25 V in a gas composition of 60 % H₂O + 40 % H₂ with steam produced from seawater and (b) the corresponding evolution of the ohmic and polarization resistance.

Similar to the investigation of the operation temperature, the influence of the steam content at the fuel electrode was studied for the utilization of steam produced from seawater. Stability tests were performed at a constant temperature of 800 °C and an applied voltage of 1.25 V.

Figure 26a illustrated the evolution of the current density. Absolute degradation rates between 25 and 139 mA·cm⁻²/24h were observed, corresponding to 1.0 to 5.8 A·cm⁻²·kh⁻¹. As discussed in chapter 6.1, these high degradation rates are attributed to the high current densities and the usage of cells from the old production batch [30-31, 123, 157].

The lowest absolute and relative degradation rates were observed for the lowest steam content 40 % ranging from 25 mA·cm⁻²/24h to 56 mA·cm⁻²/24h. Conversely, the highest steam content of 60 % resulted in the highest absolute degradation rates reaching from 84 to 139 mA·cm⁻²/24h, with relative degradation rates between 5.2 %/24h and 10.6 %/24h. A previous study on direct seawater utilization in SOECs reported similar trends for shorter test durations and lower current densities [15].

Figure 26b depicts the evolution of the ohmic and polarization resistance. While R_{Ω} remains largely unchanged throughout the test, R_p increases significantly with a higher average higher relative and absolute increase at higher steam contents.

In conclusion, R_{Ω} is not significantly affected during the degradation seen in the cells. The increase in R_p is the main contributor to the observed performance loss. A lower steam content reduces the absolute and relative degradation rates. However, by applying lower steam contents reduced current densities are accomplished at the same operating voltage. Thus, higher steam contents may be favorable in practical operation, as the increased hydrogen production rate can outweigh the elevated degradation rate.

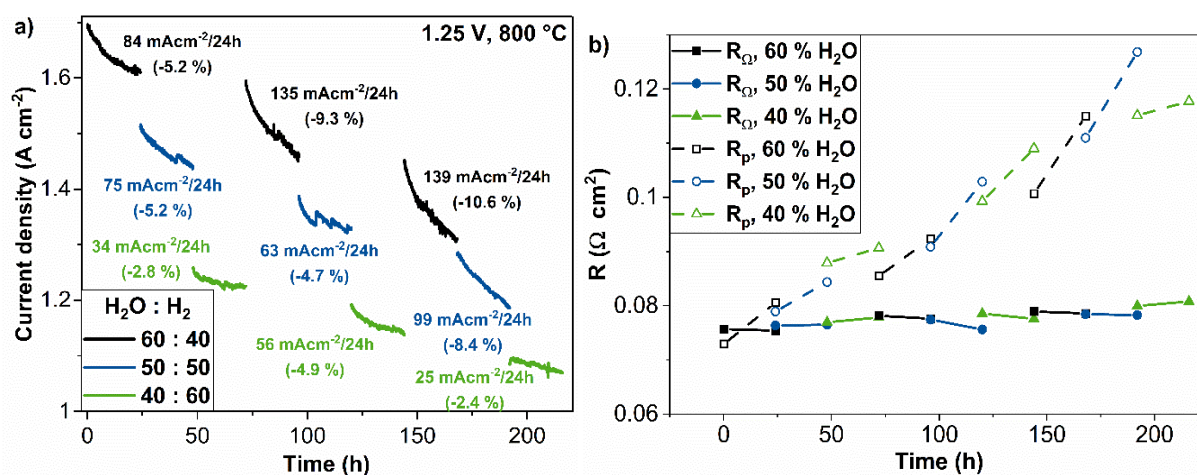


Figure 26 (a) Short time current density against time curves at different steam contents of 60 %, 50 % and 40 % with H₂ as balance gas at a constant voltage of 1.25 V and a temperature of 800 °C with steam produced from seawater and (b) the corresponding evolution of the ohmic and polarization resistance.

6.2.2.2 Long Term Stability Test – Voltage Evolution

The long term stability of a SOEC operated with steam produced from seawater is compared to a SOEC operated with steam from pure water. Experiments were conducted over 1000 hours using cells from the new production batch. The operation conditions were kept constant at 800 °C, a gas composition of 60 % H₂O + 40 % H₂ and a current load of $-1 \text{ A}\cdot\text{cm}^{-2}$. Every 100 hours of operation an EIS spectrum at OCV and an iV curve were recorded. Figure 27 shows the evolution of the cell voltage as a function of operation time. The cell measured with steam generated from pure water (pure water cell 4_{new}, see chapter 6.1) is displayed in blue and the cell operated with steam from seawater (Seawater cell 1_{new}) in green.

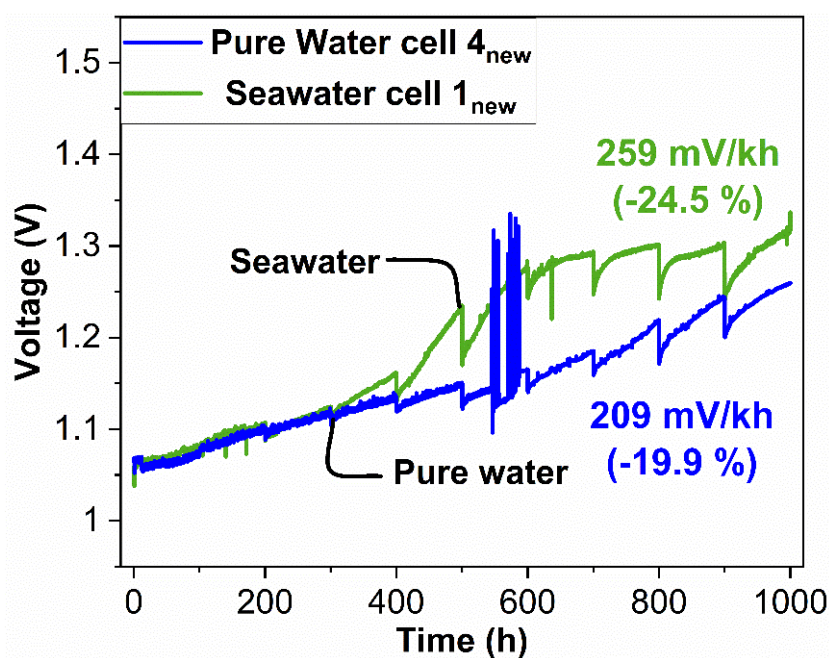


Figure 27 Voltage evolution over time for cells operated with steam generated from seawater (green) and pure water (blue) at a constant current density of $-1 \text{ A}\cdot\text{cm}^{-2}$, a temperature of 800 °C and a gas composition of 60 % H₂O + 40 % H₂.

As expected, both cells exhibit similar initial cell voltages. As noted in chapter 6.1, the voltage dips occurring every 100 hours are attributed to interruptions for electrochemical measurements of the iV curves and EIS [115-117].

Over the full 1000 hour period, degradation rates of $206 \text{ mV}\cdot\text{kh}^{-1}$ and $259 \text{ mV}\cdot\text{kh}^{-1}$ were observed for pure water cell 4_{new} and seawater cell 1_{new}, respectively. Thus, the seawater cell exhibits a slightly higher degradation rate. In addition, the evolution of the cell voltage differs between both cells. Pure water cell 4_{new} exhibits a period of linear voltage increase from 0 to 700 hours. After 700 hours the voltage increase is slightly accelerated and an increase in slope is observed. The unsteady voltage spikes in the time of 580 to 600 hours of operation are attributed to a temporary failure of the steam generation in the test setup and are not expected to influence the overall trend. In contrast, Seawater cell 1_{new} exhibits a period with a constant

linear voltage increase from 0 to 300 hours. After 300 hours until 600 hours, a steep rise in voltage is seen. In this period, the voltage increases by 0.140 V, accounting for 54 % of the total voltage rise throughout the measurement. After 600 hours until 1000 hours of operation, the voltage stabilizes, showing minimal further increase. From the results, the higher degradation rate of the seawater operated cell corresponds to the rapid voltage increase between 400 and 600 hours of operation time.

In literature, degradation rates between 16 and 129 $\text{mV}\cdot\text{kh}^{-1}$ are reported for the utilization of synthetic or real seawater which is lower compared to the measured one in this thesis of 259 $\text{mV}\cdot\text{kh}^{-1}$ [9, 14-15]. These lower rates are attributed to lower current densities used in prior work [9, 14-15]. For example, the highest reported degradation rate of 129 $\text{mV}\cdot\text{kh}^{-1}$ is reported for SOEC operation with a load of $0.3 \text{ A}\cdot\text{cm}^{-2}$ at 800 °C with a gas feed of 67 % H_2O + 33 % H_2 . [9, 14-15]. While previous studies concluded that seawater usage has no negative effect on SOEC stability [9, 15], they often lack direct comparisons to pure water operation and focus on short term degradation as discussed in chapter 4.

Thus, the differences between pure water and seawater operated cells in long term stability tests must be investigated. In particular, the sharp voltage rise between 300 and 600 hours of operation only occurring in seawater operation needs further investigation to connect the underlying degradation mechanisms unique to seawater operation.

Table 6 Degradation values and initial voltages of individual cells operated with steam generated from seawater and pure water with different operation times.

Cell Name	Operation time (h)	Water used ()	Degradation rate ($\text{mV}\cdot\text{kh}^{-1}$)	Initial voltage (V)
Pure water cell 4 _{new}	1000	Pure water	209	1.062
Seawater cell 1 _{new}	1000	Seawater	259	1.054

6.2.2.3 Long Term Stability Test – Current Density Voltage Curves

For further investigation, the iV curves recorded every 100 hours during the stability test of pure water cell 4_{new} and seawater cell 1_{new} are compared and presented in Figure 28. The current densities decrease continuously in the case of seawater cell 1_{new} until 600 hours of operation. Between 600 and 900 hours, the iV curves exhibit similar shapes and current density values, indicating a stabilization in performance. A slight decrease in current densities is observed in the iV curve at 1000 hours of operation. After 400 hours of operation, the iV curves exhibit a sigmoidal shape and hysteresis develop. The forward scans exhibit higher current densities, and the backward scans lower current densities. As shown in Figure 28a, the same

trends are visible for the pure water operated cell, indicating that the hysteresis and sigmoidal shape are not specific to seawater usage.

The trends seen here for the seawater and pure water operated cells are reported in the literature for various operation conditions of SOCs. [17, 31, 127-129] For instance, Dittrich connected the hysteresis to structural changes in the cell in her thesis, which would explain the observation after a certain stability test time [17]. However, a clear identification of hysteresis must be considered in the future.

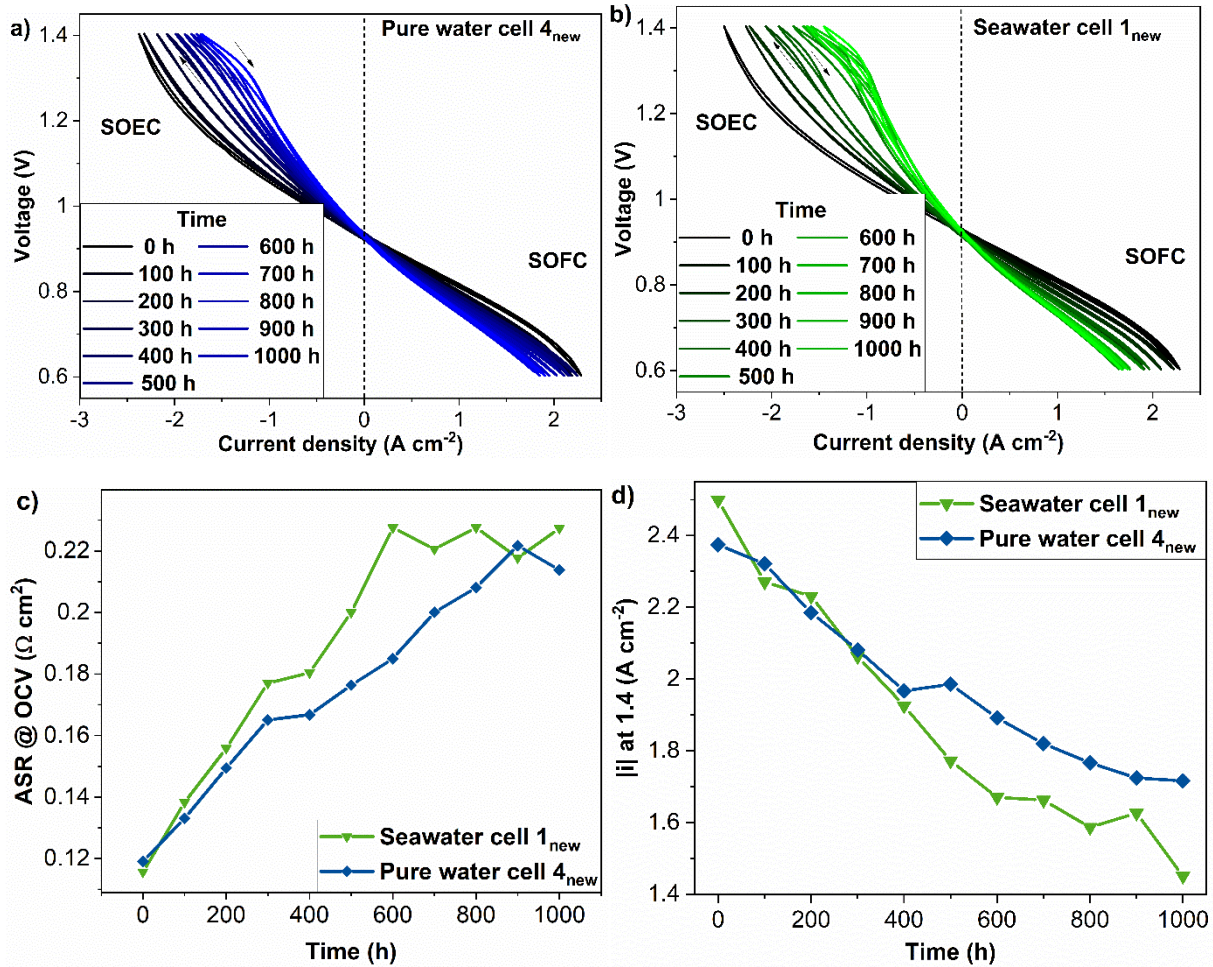


Figure 28 iV curves recorded every 100 hours of operation (a) of pure water cell 4_{new} operated for 1000 hours and (b) of seawater cell 1_{new} operated for 1000 hours. Evaluation of the (c) ASR at OCV and (d) the current density at 1.4 V for both cells.

In the next step, the evolution of the ASR at OCV, derived from the iV curves, is compared to seawater cell 1_{new} and pure water cell 4_{new}. Figure 28c presents the evolution of the Asr for both cells. Seawater cell 1_{new} shows an increase in ASR at OCV until 600 hours of operation. 6.2.2.2.1. The initial ASR increases from an initial value of 116 mΩ·cm² to 227 mΩ·cm² after 1000 hours of operation. In contrast, pure water cell 4_{new} exhibits a steady increase in ASR over the entire operation, from 119 mΩ·cm² to 214 mΩ·cm². Interestingly, the ASR at OCV is

similar for both cells at the end of the stability measurement which contrasts with the voltage evolution seen in Figure 27. Thus, this observation suggests that ASR at OCV alone may not fully capture the differences in degradation behavior.

Figure 28d illustrates the current densities of both cells at a voltage of 1.4 V as a function of the degradation time. As discussed in chapter 6.1 the current density at 1.4 V of pure water cell 4_{new} is steadily decreasing. Similarly, seawater cell 1_{new} follows a constant decrease in current density for the operation time from 0 to 400 hours, which matches the behavior in pure water cell 4_{new}. However, between 400 and 600 hours, seawater cell 1_{new} shows a more pronounced drop in current density ($0.254 \text{ A}\cdot\text{cm}^{-2}$) compared to pure water cell ($0.076 \text{ A}\cdot\text{cm}^{-2}$) during the same period. After 600 hours, the current densities of the seawater operated cell remain relatively stable until 900 hours. After 900 hours a minor decrease is observed until the end of the measurement.

At the end of the measurement the current density of pure water cell 4_{new} is higher compared to seawater cell 1_{new} which is consistent with the voltage evolution seen in Figure 27. In addition, the overall degradation trends of both cells correlate well with the evolution of ASR at OCV. However, both cells exhibit a similar ASR at OCV at the end of the measurement whereas pure water cell 4_{new} shows a higher current density at 1.4 V. This indicates that voltage dependent electrochemical processes that are not captured at OCV are contributing to the degradation and differ between both cells [159-160].

6.2.2.4 Long Term Stability Test – Electrochemical Impedance Spectroscopy

EIS measurements were performed every 100 hours throughout the 1000 hour stability experiment. Figure 29a shows the Nyquist plots for pure water cell 4_{new} and Figure 29b for seawater cell 1_{new}. In both cells, the high frequency regime exhibits an inductive behavior, which is attributed to wiring effects, as commonly reported in the literature [31, 51].

Pure water cell 4_{new} exhibits a slight increase of the high frequency intercept with the real impedance axis over the entire measurement time. In comparison, the increase is more pronounced in the Nyquist plots of seawater cell 1_{new}. However, direct interpretations of the high frequency ohmic (serial) resistance are difficult due to the parasitic inductance present [51].

A more pronounced and reliable trend is observed at the low frequency intercept with the real axis, which increases significantly for both cells. Thus, the dominant contribution to the degradation originates from an increase in polarization resistance.

Furthermore, the low frequency interception with the real axis increases due to a shift of the semi circles in the high to intermediate frequency region to higher resistance values in both cells. In pure water cell 4_{new} a similar increase occurs gradually and consistently over time. In contrast, seawater cell 1_{new} shows a rapid increase in the high to intermediate frequency

related resistances between 300 and 600 hours of operation which corresponds to the sharp voltage increase in this period previously discussed in chapter 6.2.2.2.

This trend is further supported by the distribution of relaxation times (DRT) analysis derived from the EIS data, shown in Figure 29c and Figure 29d. in both cells, the contributions at low relaxation frequencies between 1 to 100 Hz exhibit only minor changes in magnitude. The processes referring to the intermediate (300 to 1000 Hz) and the high frequency (3000 Hz) regimes increase significantly in magnitude. Furthermore, seawater cell 1_{new} shows a sharp increase in these contributions between 400 and 600 hours, which is not observed in pure water cell 4_{new}.

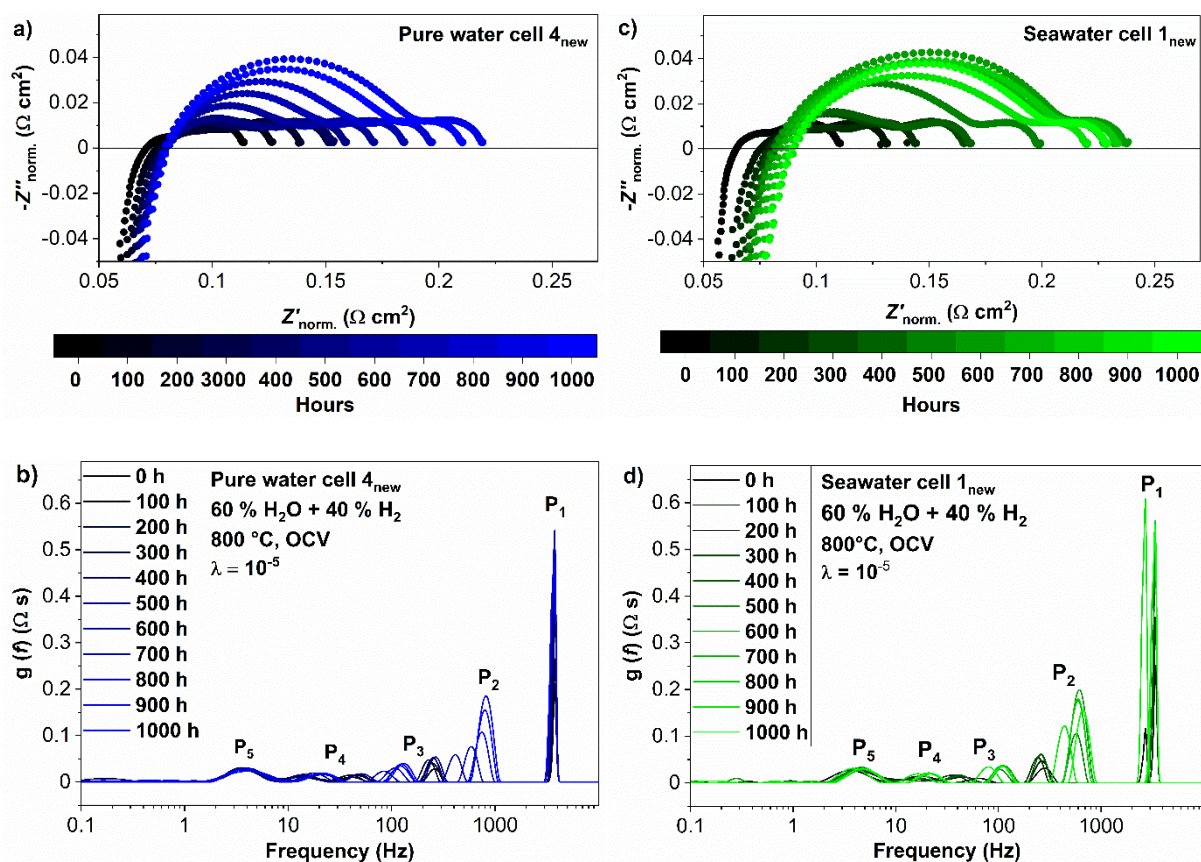


Figure 29 Nyquist plots and DRT spectra of the EIS data recorded at OCV every 100 hours during the stability test for (a, b) pure water cell 4_{new} and (c, d) seawater cell 1_{new} operated for 1000 hours.

To achieve a clear deconvolution of the ohmic and polarization contribution as well as insights into the underlying electrochemical processes, the EIS data were fitted using the equivalent circuit model developed in chapter 6.1.1.3. The fitting of the EIS data enabled the determination of R_{Ω} and R_p at OCV. For a comprehensive evaluation, the results from the seawater stability test (seawater cell 1_{new}) are compared to those from the pure water operation (pure water cell 4_{new}).

Figure 30a presents the evolution of R_Ω over time for both cells. As earlier shown in chapter 6.1, pure water cell 4_{new} maintains a nearly constant R_Ω throughout the measurement. In contrast, seawater cell 1_{new} exhibits a slight increase in R_Ω by $0.013 \Omega \cdot \text{cm}^{-2}$ from an initial value of $0.057 \Omega \cdot \text{cm}^{-2}$ to $0.070 \Omega \cdot \text{cm}^{-2}$.

Figure 30b shows the corresponding evolution of R_p . In seawater cell 1_{new}, R_p increases gradually by $0.051 \Omega \cdot \text{cm}^{-2}$ during the first 400 hours of operation. The rise in R_p is accelerated between 400 to 600 hours where an increase of $0.074 \Omega \cdot \text{cm}^{-2}$ is observed. From 600 to 1000 hours, R_p stabilizes or even shows a slight decrease. In contrast, pure water cell 4_{new} exhibits a steady and continuous increase in R_p throughout the full measurement period.

These trends correlate with the voltage time evolution discussed earlier in Section 6.2.2.2 and the analysis of the Nyquist and DRT plots shown above. In both cells, the degradation is dominantly covered by the increase in R_p . The rapid increase in voltage between 400 and 600 hours observed in seawater cell 1_{new} is mainly due to an increase in R_p .

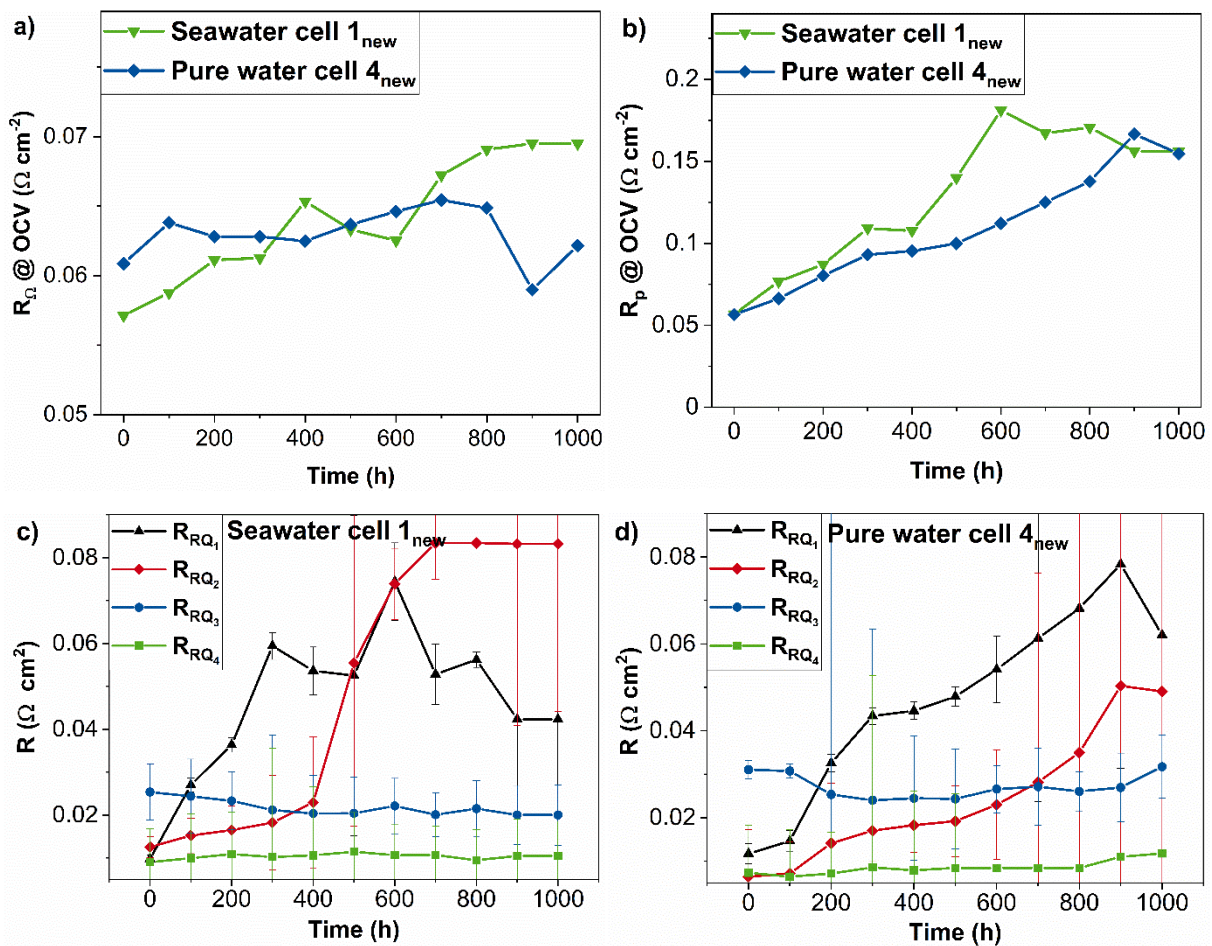


Figure 30 Evolution of (a) the ohmic resistance and (b) the polarization resistance for cells operated with steam generated from seawater and pure water and the evolution of the individual process resistances for the (c) seawater cell 1_{new} and (d) pure water cell 4_{new}. All data shown is derived from the ECM fitting of the EIS data recorded every 100 hours during the stability measurement at OCV.

Interestingly, like the ASR at OCV discussed in the previous section, R_p is similar between seawater cell 1_{new} and pure water cell 4_{new} at the end of the stability test. However, seawater cell 1_{new} still exhibits a higher operating voltage at 1 A·cm⁻², as shown in chapter 6.2.2.2. As stated before in chapter 6.2.2.3, this indicates underlying differences in individual voltage dependent processes in both cells. By breaking down R_p to its individual resistance contributions the differences between seawater and pure water operation are further investigated.

Next, the evolution of the individual resistances derived from the ECM fitting are discussed. An ECM containing an inductance in series with a resistor and four RQ elements is used as discussed in chapter 6.1. In Figure 30c and Figure 30d, the individual resistances of the RQ elements of both cells are shown.

In both cells, R_{RQ4} remains largely unaffected by the operation time. The low frequency process (2 - 9 Hz) associated with RQ_4 has been attributed to the gas diffusion at the Ni/YSZ fuel electrode through literature studies due to its temperature independence and dependence on a variation of fuel gas content [62, 118, 130].

Like R_{RQ4} , R_{RQ3} exhibit no significant change during the test duration in either cell. In the literature, the intermediate frequency process of around 10 Hz RQ_3 is attributed to the air electrode due to its dependency on the oxygen content at the LSC air electrode [62, 130].

In contrast, the resistance R_{RQ2} increases substantially in both cells over time. In pure water cell 4_{new}, a steady rise of R_{RQ2} is observed from 7 to 49 mΩ·cm² over the measurement time. In seawater cell 1_{new}, R_{RQ2} increases more pronounced from 11 to 83 mΩ·cm². The increase of R_{RQ2} in seawater cell 1_{new}, is gradual during the first 300 hours of the measurement. After 300 to 600 hours R_{RQ2} increases sharply. After 600 to 1000 hours, the resistance stays at a constant value. This trend mirrors the overall polarization resistance behavior and thus in seawater cell 1_{new} R_{RQ2} is the dominant contribution to the R_p increase. This behavior is not visible in pure water cell 4_{new}. Overall significant differences between both cells are registered in the evolution and total increase of R_{RQ2} . Based on previous literature, RQ_2 is associated with a process at the Ni/YSZ fuel electrode due to its dependence on the fuel gas content [61, 118, 130-131]. It is reported that RQ_2 is assigned to the charge transfer reaction in the Ni-YSZ fuel electrode [61].

The last contribution R_{RQ1} is attributed as a fuel electrode process contributing to the electrochemical reaction in the Ni-YSZ fuel electrode including the O²⁻ transport (see chapter 3.2.3). In seawater cell 1_{new}, R_{RQ1} increases sharply during the first 300 hours of operation followed by a slight decrease in value. A similar rapid increase of R_{RQ1} is observed in the first 300 hours in pure water cell 4_{new}. However, unlike the seawater cell, R_{RQ1} steadily increases from 300 hours onwards until the end of the operation at 1000 hours in pure water cell 4_{new}. In

addition, R_{RQ1} is the main contributor to the increase in R_p in pure water cell 4_{new}, while in seawater cell 1_{new} R_{RQ1} levels off after the initial rise.

Since both R_{RQ1} and R_{RQ2} are attributed to processes at the Ni-YSZ fuel electrode, changes in the fuel electrode are the primary contributors to the overall degradation in both cells. For visualization purposes, the resistive contributions from the fuel electrode, air electrode, and ohmic resistance are visualized for seawater cell 1_{new} and pure water cell 4_{new} in Figure 31a and Figure 31b, respectively.

In conclusion, R_{RQ1} is the main contribution to the increase in R_p in pure water cell 4_{new} whereas R_{RQ2} is the main contribution to the increase in R_p in seawater cell 1_{new}. The sharp voltage rise between 400 and 600 hours in seawater cell 1_{new} as discussed in chapter 6.2.2.2 is due to an increase in R_{RQ2} and thus points to electrochemical degradation processes specific to the Ni-YSZ fuel electrode. This behavior is not seen in pure water cell 4_{new}, implying that different degradation mechanisms are occurring during the stability test in both cells.

In pure water cell 4_{new} the gradual increase in R_{RQ1} indicates that microstructural changes in the Ni-YSZ fuel electrode are negatively affecting the electrochemical reaction and especially the O^{2-} transport. In contrast, the sharp increase in R_{RQ2} in seawater cell 1_{new} is connected to the charge transfer in the Ni-YSZ fuel electrode and indicates degradation related to Ni agglomeration, depletion or poisoning of the Ni-YSZ fuel electrode. The poisoning of the fuel electrode is potentially related to impurity transport from seawater to the cell. Thus, the transport of impurities and differences in the microstructures after operation are investigated by post test characterization of both cells in the following.

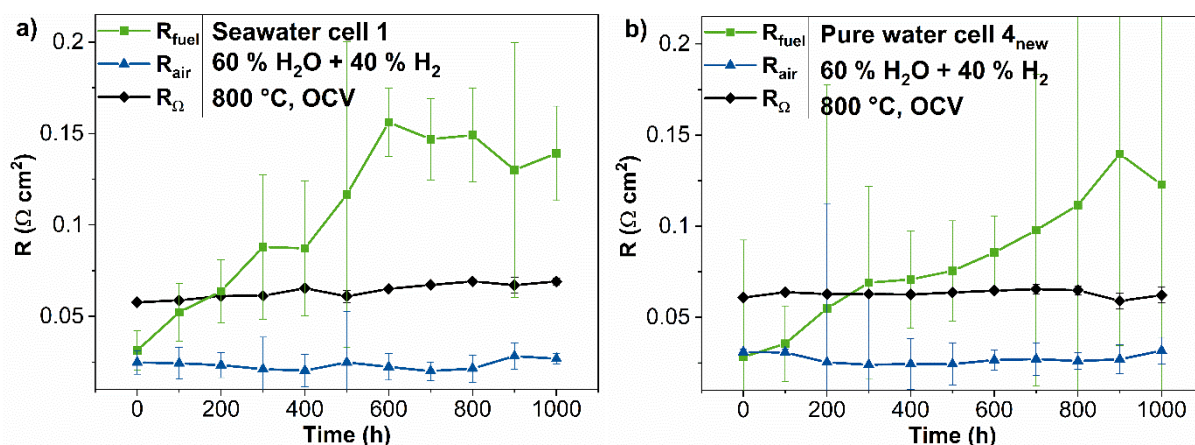


Figure 31 Evolution of the R_{Ω} , the resistance corresponding to the Ni-YSZ fuel electrode and the resistance corresponding to the LSC air electrode for (a) seawater cell 1_{new} and (b) pure water cell 4_{new}.

6.2.2.5 Long Term Stability Test – Post Test Characterization

The surface of the Ni-YSZ fuel electrode was characterized by X-ray diffraction (XRD) measurements to identify possible crystalline impurities. Figure 32a compares the respective

XRD spectra recorded of the fuel electrode surface of seawater cell 1_{new} and pure water cell 4_{new}. Both spectra exhibit only the characteristic reflections of Ni and YSZ and no additional diffraction peaks indicate impurities at surface of the fuel electrode. Furthermore, no significant differences between the XRD spectra of seawater cell 1_{new} and pure water cell 4_{new} are identified.

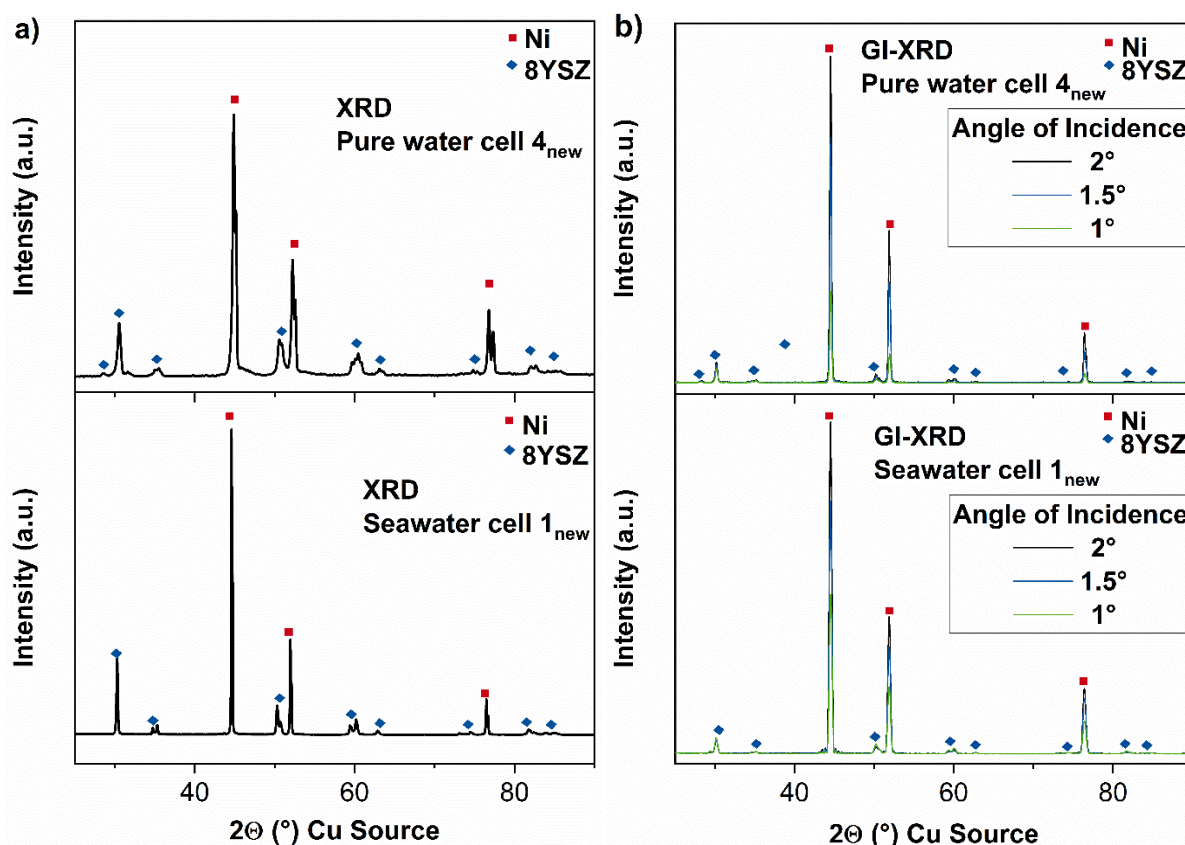


Figure 32 (a) XRD spectra and (b) GI-XRD spectra of the Ni-YSZ fuel electrode surface of the pure water cell 4_{new} and seawater cell 1_{new}. Both cells were characterized after disassembly from the measurement setup and exposure to air at room temperature.

For enhanced surface resolution and improved detection of minor crystalline impurities present on the Ni-YSZ fuel electrode surface, grazing incidence XRD (GI-XRD) measurements were conducted. Figure 32b shows the respective GI-XRD spectra for pure water cell 4_{new} and seawater cell 1_{new}. In both cells, only peaks corresponding to the Ni and YSZ phases are identified. In the GI-XRD measurements, the relative intensity of Ni peaks is increased due to the thin Ni contact layer printed on top of the Ni-YSZ fuel electrode which dominates the lower penetration depth of the GI-XRD measurements. Importantly like in the conventional XRD measurement, no crystalline salt deposits or additional impurity phases are detected on the Ni-YSZ fuel electrode surface of seawater cell 1_{new}. This indicates that impurities transported by seawater usage are either amorphous, present in concentrations below the detection limit, or not retained on the surface in crystalline form.

To further investigate surface deposits, seawater cell 1_{new} was analyzed by scanning electron microscopy (SEM). Figure 33 presents two representative SEM images of the Ni-YSZ fuel electrode surface of seawater cell 1_{new}. Numerous nanoscale particles of varying morphology are observed on top of the current collecting Ni layer. For comparison, SEM images at the same position of pure water cell 4_{new} are provided in Figure A 3 in the appendix, revealing similar particles on top of the Ni-YSZ fuel electrode surface. Therefore, based on SEM imaging alone no distinct salt deposits or additional surface deposits are identified on the Ni-YSZ fuel electrode surface of seawater cell 1_{new}.

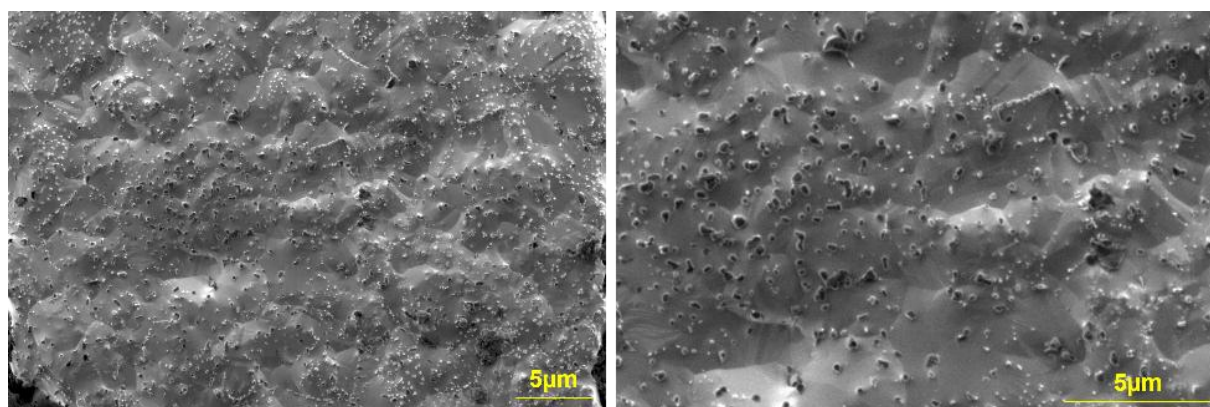


Figure 33 Top view of a Ni-YSZ fuel electrode surface of seawater cell 1_{new} operated for 1000 hours with steam produced from seawater.

To elucidate the nature of these surface particles, SEM-EDX mapping was conducted. Most of the particles found on the surface of seawater cell 1_{new} were identified as Al₂O₃ particles or ZrO₂ particles as shown in Figure A 4 in the appendix. The presence of ZrO₂ particles can be attributed to the 8-YSZ phase in the Ni-YSZ fuel electrode itself. The presence of Al is likely associated with the use of alumina containing components in the test setup. In addition, alumina is often used as a sintering aid for shaping the sintering behavior of ceramics, which may contribute to its presence on the electrode surface [161].

In some localized regions of the Ni-YSZ fuel electrode surface of seawater cell 1_{new}, CaO_x deposits were detected as shown in the SEM-EDX maps in Figure 34. However, no Na containing impurities were found on the Ni-YSZ fuel electrode surface of seawater cell 1_{new}. By calculations based on prior research, it is estimated that during 1000 hours of seawater operation an amount of 2 mg NaCl and 0.2 mg Ca containing species could be transported to seawater cell 1_{new} [14, 162]. In the present thesis, only Ca species were detected across several spots on the Ni-YSZ fuel electrode surface. Although Na species were not detected by SEM-EDX it cannot be ruled out that Na is deposited on the surface of the Ni-YSZ fuel electrode. While Salt deposits on the fuel electrode surface could potentially interfere with the electrical contact and performance of the SOECs, the EIS measurements discussed in chapter

6.2.2.4 show no notable increase in R_{Ω} for seawater cell 1_{new}. Thus, no significant influence is expected by the salt deposits on the Ni-YSZ electrode surface.

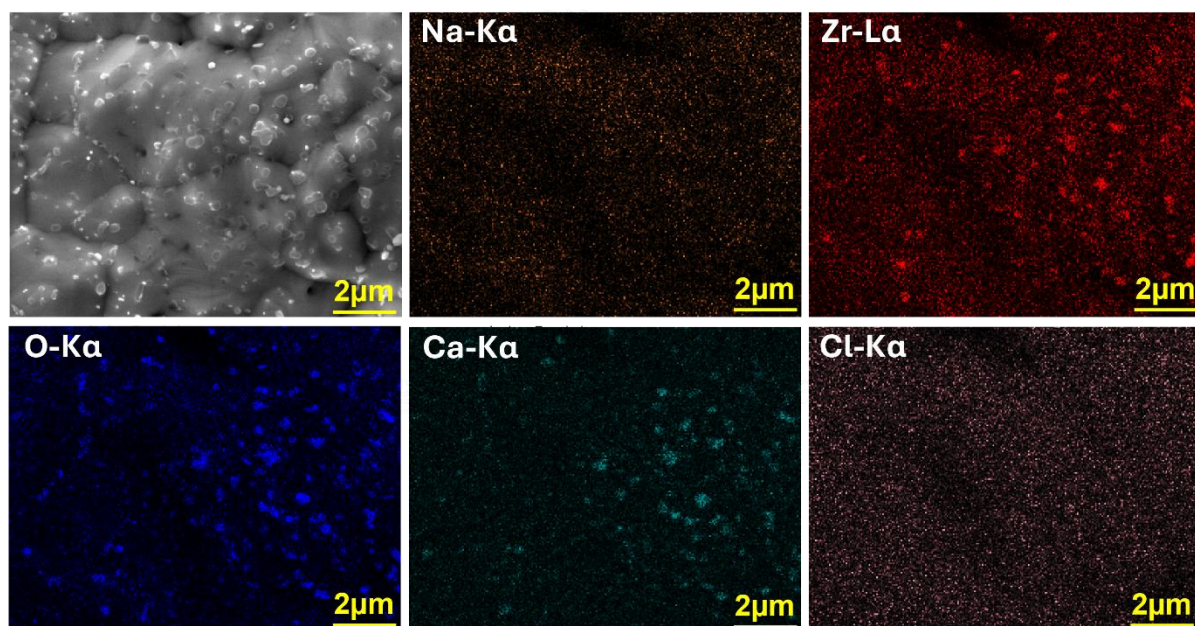


Figure 34 SEM-EDX analysis of the Ni-YSZ fuel electrode surface of seawater cell 1_{new} operated for 1000 hours with steam produced from seawater.

The cross section of the Ni-YSZ fuel electrode was investigated to assess potential microstructural changes and deposits in the electrochemical active porous electrode. Initially, the fractured cross sections of the active layers were analyzed, as shown in Figure 35. As the cells are fractured by hand, the resulting surfaces are uneven and may introduce artifacts.

In the case of seawater cell 1_{new}, small nanoparticles are observed on the surfaces of some grains within the active layer of the Ni-YSZ fuel electrode. In contrast, these nanoparticles are absent in the freshly reduced reference sample and in pure water cell 4_{new}. As discussed in chapter 6.1, such nanoparticles have been identified as ZrO₂ particles deposited on Ni grains in the fuel electrode active layer. Since SEM-EDX mapping of the Ni-YSZ fuel electrode surface confirmed the transport of salt to seawater cell 1_{new} during operation it cannot be excluded that some of the nanoparticles are due to seawater operation and consist of salt residues or other impurities.

For clarification, SEM-EDX measurements were performed on fractured cross sections of the Ni-YSZ electrode in seawater cell 1_{new}. Figure 36 and Figure 37 display two EDX maps from two distinct areas of the fractured cross sections of seawater cell 1_{new}. In both cases, beam induced damage occurred during the mapping which made detailed analysis difficult and limited the spatial resolution and accuracy. Notably, similar beam damage was encountered during SEM-EDX measurements of pure water cell 4_{new}, indicating that this observation is not a consequence of seawater utilization. The expected elemental Ni, Zr, and O maps are visible

in the upper parts of both figures (Figure 36 and Figure 37). Additional minor element signals of impurities are presented in the lower parts.

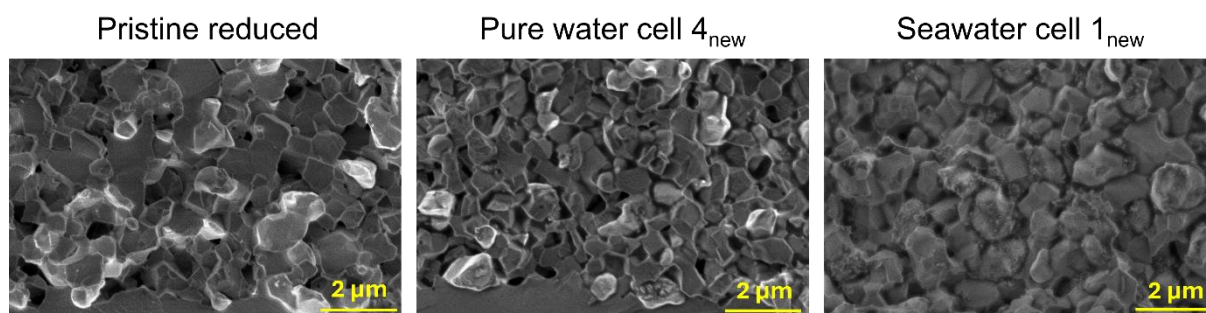


Figure 35 SEM images of the fractured Ni-YSZ fuel electrode cross section of a pristine reduced, a cell operated for 1000 hours with pure water for steam generation, and a cell operated for 1000 hours with seawater for steam generation.

From the EDX mapping, no evidence of Cl containing impurities in the Ni-YSZ fuel electrode is identified. Similarly, the Ca maps showed no clear indication of Ca based deposits within the active layer. However, in the case of Na, small and localized particles were detected in the corresponding Na elemental map. Interestingly, these Na signals overlap with the carbon signals in the carbon EDX elemental maps suggesting a Na and C containing compounds, possibly carbonates or organic sodium salts.

This observation indicates the transport and deposition of Na containing impurities within the electrochemically active layer of the fuel electrode during seawater operation. To the best of the author's knowledge, the impact of sodium containing impurities as deposited particles within Ni-YSZ fuel electrodes has not been evaluated in the literature. However, potential blocking of active sites and pore structures by such impurities is plausible and could be critical to the SOEC lifetime.

In summary, the results demonstrated that different impurities, namely Na and Ca species, are transported to the SOEC during seawater operation where they are deposited either in the cross section or on the surface of the Ni-YSZ fuel electrode. This contradicts earlier studies on seawater utilization in SOECs, which reported no impurity deposits at the fuel electrode [9, 14-15, 94]. The discrepancy is likely due to the shorter test durations and the limited scope of post test characterization in those previous studies, as discussed in chapter 4.

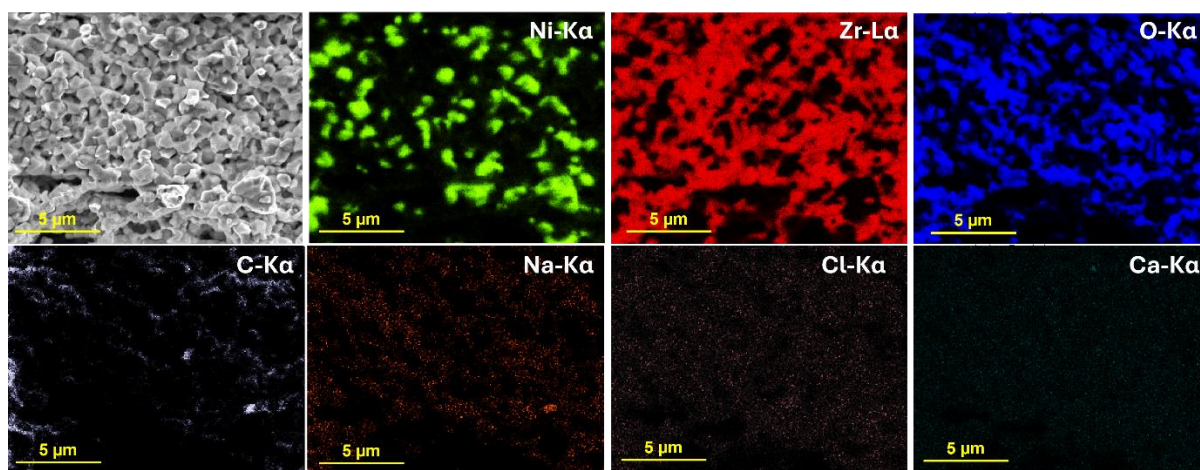


Figure 36 SEM-EDX maps of the Ni-YSZ fuel electrode fractured cross section of seawater cell 1_{new} (spot 1) operated with steam generated from seawater for 1000 hours.

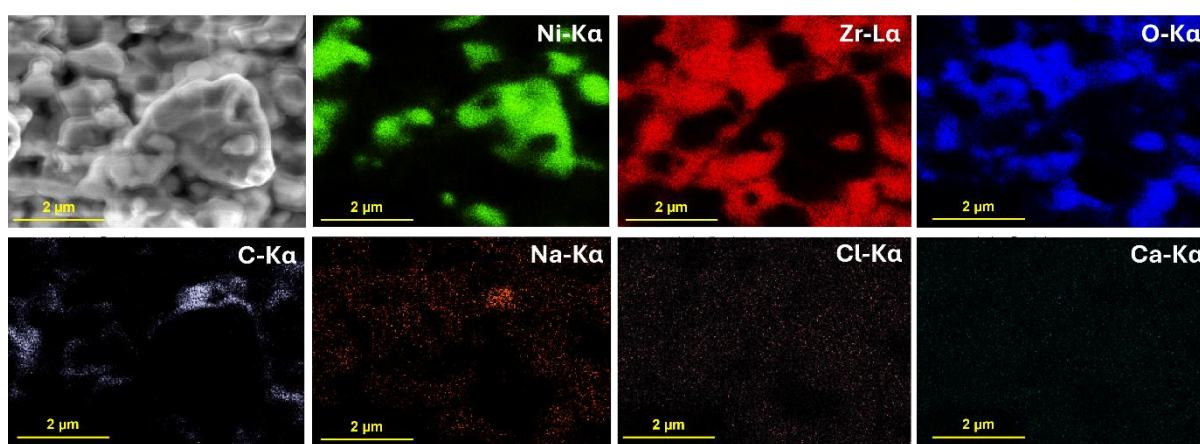


Figure 37 SEM-EDX maps of the Ni-YSZ fuel electrode fractured cross section of seawater cell 1_{new} (spot 2) operated with steam generated from seawater for 1000 hours.

By embedding, polishing and consecutive sputtering with gold of the fractured cross section the beam damage previously examined is avoided. This approach enabled analysis of a flat and stable cross section, allowing clearer identification of microstructural features in the Ni-YSZ fuel electrode. However, it should be noted that embedding and water based polishing might lead to washing out salt impurities and the potential introduction of artifacts from the used resin. The polished cross section SEM images of the fuel electrode of both cells are primarily evaluated to assess conventional microstructural degradation mechanisms (see chapter 2.3).

Figure 38a presents the gold sputtered, polished cross sections of the Ni-YSZ electrode of a pristine reduced cell, seawater cell 1_{new} and pure water cell 4_{new}. All cells show good adhesion between the Ni-YSZ fuel electrode and the YSZ electrolyte. The denser active Ni-YSZ layer adjacent to the electrolyte is clearly distinguishable from the more porous support structure above in both cells. No significant structural separation or delamination between the individual

layers is depicted for seawater cell 1_{new} and pure water cell 4_{new}. In addition, both cells exhibit no delamination of the LSC air electrode as shown in Figure A 5, indicating mechanical integrity after operation.

A slight densification of the active Ni-YSZ fuel electrode layer is qualitatively observed in pure water cell 4_{new}. In contrast, Seawater cell 1_{new} shows no significant densification of the active Ni-YSZ fuel electrode. This hints towards distinct microstructural evolution paths depending on the steam source used during operation.

In seawater cell 1_{new}, small gaps between the Ni and YSZ phases are seen within the dense active layer of the Ni-YSZ fuel electrode. These features are highlighted by red arrows in the SEM image (Figure 38a). Additionally, small black inclusions within the Ni particles are visible in the dense active layer of the fuel electrode. These are marked by red squares in the SEM image. Both features are absent in the corresponding SEM image of pure water cell 4_{new}. The gaps near the Ni-YSZ electrode/electrolyte in seawater cell 1_{new} correlate with the slight increase in R_{Ω} discussed in section 6.2.2.4. These gaps disrupt the percolating electronic and ionic pathways within the Ni-YSZ electrode, resulting in inactivity of active sites and an artificial increase in the effective thickness of the not non electrochemically active 8-YSZ electrolyte.

EDX line scans performed on the Ni particles in seawater cell 1_{new} reveal that the black inclusions correspond to Si oxides as shown in Figure 38b by the increase in Si-L α and O-K α signals at the location of incorporation. This is in accordance with the results shown in chapter 6.1 and with literature reports [126]. The incorporation mechanism of Si into Ni particles is discussed in more detail in references [33, 135].

Since both cells originate from the same production batch the presence of Si contaminants in seawater cell 1_{new} are attributed to the use of seawater. As described in the literature natural seawater contains approximately a Si content of around 0.4 mg/L and a similar content is expected for the seawater used in this work [14]. Notably, even ultrapure water with a content of 7 μ g/L of Si has been shown to result in Si contamination of Ni based fuel electrodes [163]. The detection of Si incorporation in the Ni-YSZ fuel electrode during seawater operation has not been reported in previous on SOECs operated with seawater [9, 14-15, 94]. In the case of synthetic seawater usage only the salt contents are considered which explains the contradictory results [9]. As outlined in chapter 4, prior studies also often lack rigorous comparisons with pure water operation and systematic post test characterization. This leads to a potentially overlooking of small changes in the electrode microstructure like black incorporations. In the author's opinion these two factors explain why Si poisoning of the Ni-YSZ fuel electrode has not been reported in other literature studies in the context of seawater utilization in SOECs.

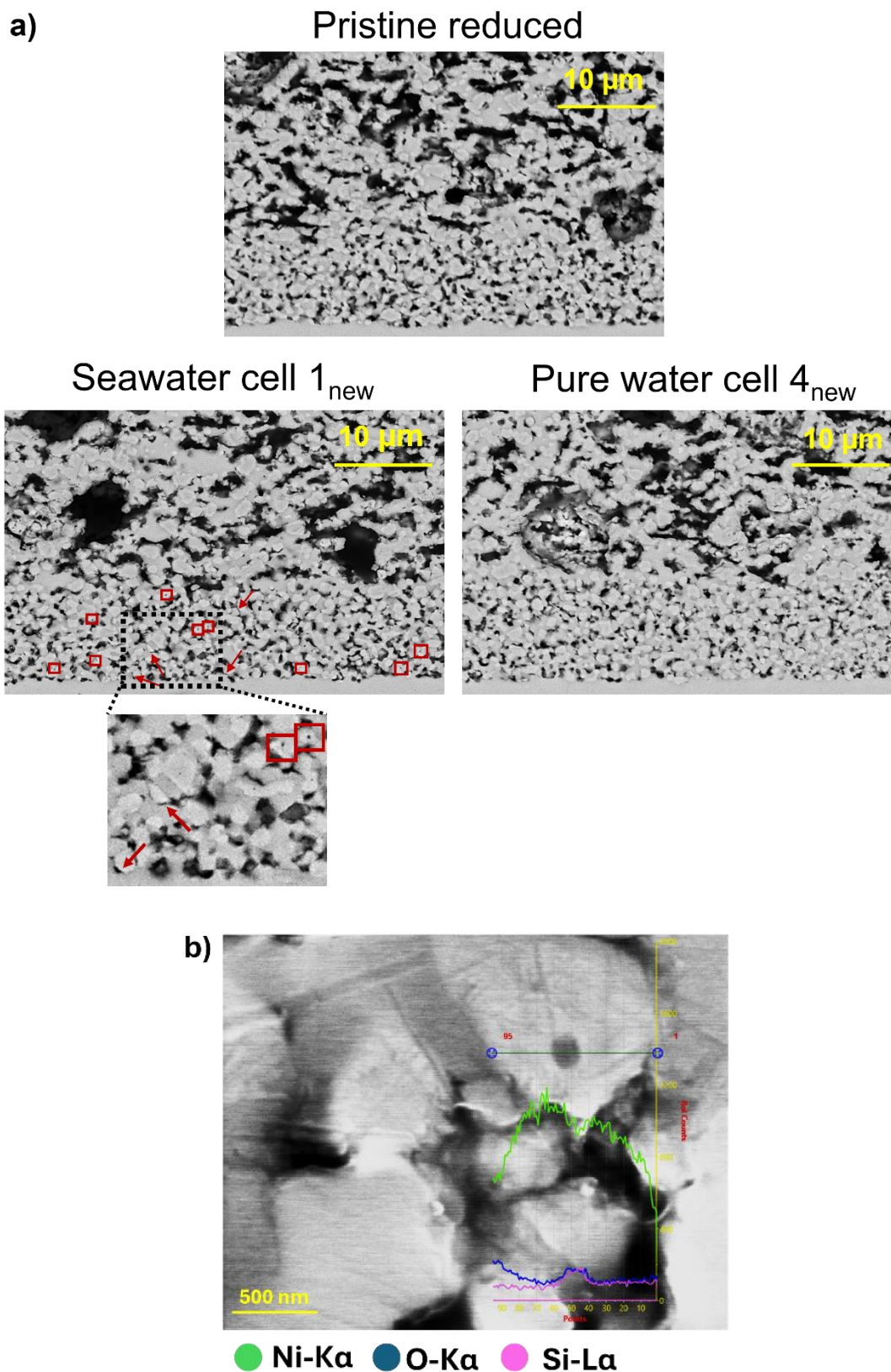


Figure 38 SEM images showing the embedded and polished cross section of the Ni-YSZ electrode of a pristine reduced cell, pure water cell 4_{new} and seawater cell 1_{new}. Red arrows indicate gaps between the Ni and YSZ phases, while red squares mark inclusions within the Ni particles. (b) SEM-EDX analysis of a Ni particle in the Ni-YSZ active layer of seawater cell 1_{new}.

To further evaluate the microstructural evolution in the Ni-YSZ fuel electrode of both cells, EDX maps of Ni and Zr were recorded and are presented in Figure 39. For comparison, a pristine reduced cell was additionally analyzed.

In the pristine reduced cell, the Ni phase appears homogeneous and well interconnected with small, uniformly distributed Ni particles in the dense active layer adjacent to the electrolyte. Similarly, the Zr phase is fine structured, indicating a well developed percolating porous network. These microstructural features are also observed in seawater cell 1_{new} where no significant deviations from the pristine reduced cell are visible. Specifically, no signs of Ni agglomeration or migration are visible which are mechanisms known to contribute to degradation in SOECs as described in chapter 2.3 [1, 29, 124]. Additionally, in pure water cell 4_{new} no pronounced Ni agglomeration in the dense active layer is visible, however, a densification of the Zr phase is observed. These observations explain the qualitative densification of the active Ni-YSZ fuel electrode layer seen earlier in pure water cell 4_{new} after 1000 hours of operation (Figure 38).

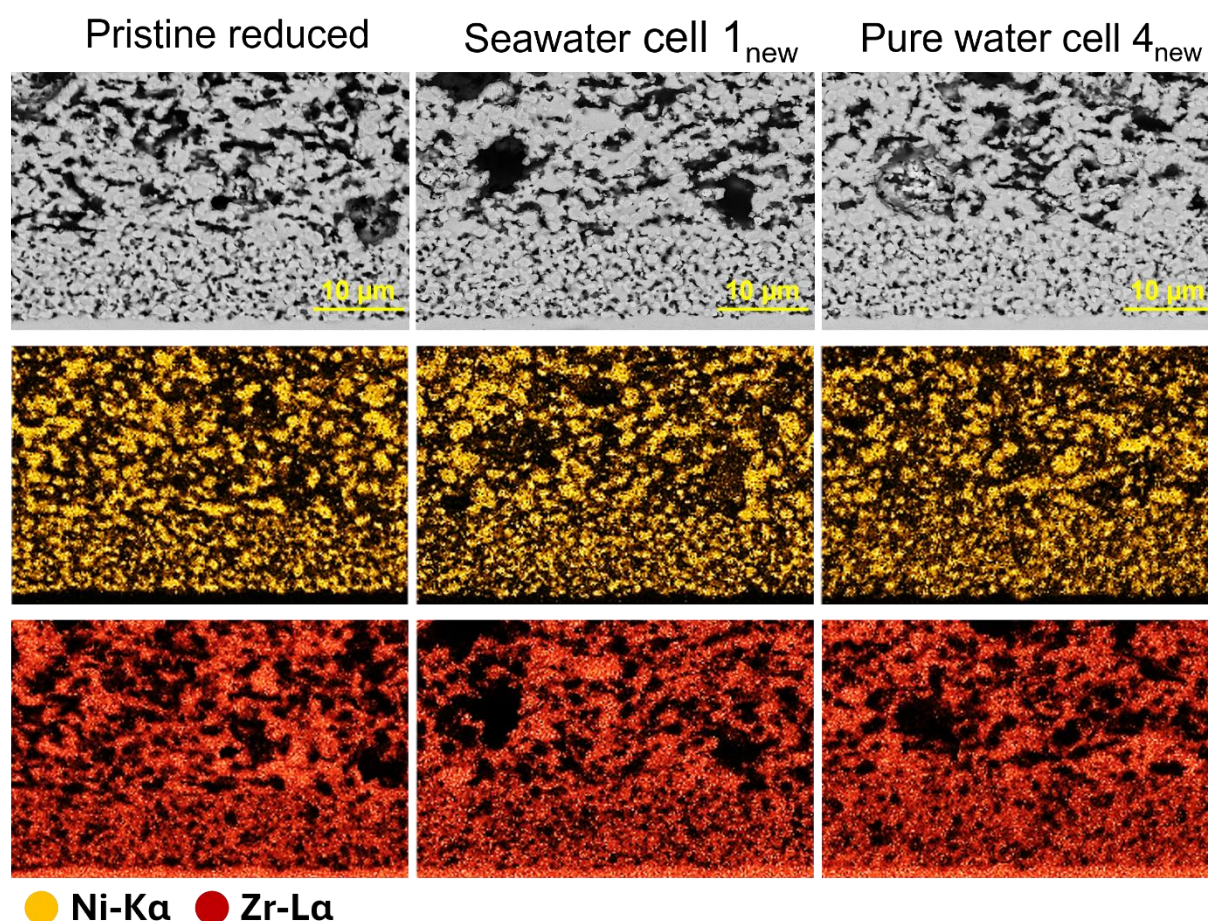


Figure 39 SEM-EDX analysis of the Ni-YSZ fuel electrode of a pristine reduced cell, pure water cell 4_{new} and seawater cell 1_{new} operated for 1000 hours in steam electrolysis mode.

Table 7 summarizes the relative content of Ni, Zr and porosity in the Ni-YSZ fuel electrode active and support layer, derived from the SEM-EDX measurements. Both cells exhibit no significant Ni depletion compared to the pristine reduced cell in the active Ni-YSZ fuel electrode layer adjacent to the electrolyte. Pure water cell 4_{new} shows an increase in Zr fraction, consistent with the observed qualitative Zr phase densification. This densification is not present in seawater cell 1_{new}.

Moreover, average particle sizes of Ni and Zr are provided in Table 7. Both operated cells exhibit slightly increased Ni particle sizes in the active Ni-YSZ fuel electrode layer compared to the pristine cell, with no significant difference between pure and seawater operation. Interestingly, pure water cell 4_{new} shows a substantial increase in Zr particle size, while seawater cell 1_{new} maintains a particle size distribution comparable to the pristine reduced cell. These findings suggest that operation with seawater suppresses a Zr densification in the active fuel electrode layer and may contribute to stabilizing the YSZ phase in the Ni-YSZ fuel electrode. In contrast, a densification of the Zr phase as observed in pure water operation could lead to a reduction of the electrochemically active triple phase boundary (TPB) length, negatively impacting cell performance, as discussed in chapter 6.1.

Table 7 Quantitative analysis using the SEM/EDX images for the active functional layer and support layer of the Ni-YSZ fuel electrode.

Fraction	Pristine active layer	Pristine support layer	Pure water cell 4 _{new} active layer	Pure water cell 4 _{new} support layer	Seawater cell 1 _{new} active layer	Seawater cell 1 _{new} support layer
Porosity	28 %	39 %	22 %	32 %	26 %	30 %
Ni fraction	30 %	27 %	31 %	27 %	30 %	27 %
Zr fraction	42 %	34 %	47 %	41 %	44 %	44 %
Average						
Ni particle size	0.97 µm	1.09 µm	0.99 µm	1.06 µm	0.99 µm	1.03 µm
Average						
Zr particle size	1.12 µm	1.39 µm	1.31 µm	1.42 µm	1.12 µm	1.42 µm

Comparing seawater and pure water operation, distinct differences in the microstructural evolution were observed that correlate with the differences in voltage evolution and electrode processes identified through EIS analysis in chapter 6.2.2.4. As discussed, different

degradation mechanisms and processes in the Ni-YSZ fuel electrode dominate the long term performance of pure water and seawater operation.

In pure water cell 4_{new}, a continuous increase in the resistances R_{RQ1} and R_{RQ2} was recorded, with R_{RQ1} being the dominant contributor to the steady rise in operation voltage during the stability test. The respective processes were attributed to the electrochemical reaction at the Ni-YSZ fuel electrode and the ion transport within the ionic YSZ network. This correlates with the observed agglomeration of the Zr phase and the slight agglomeration of the Ni phase in pure water cell 4_{new} as both reduce the triple phase boundary (TPB) length, the ionic conductive pathways in the percolating YSZ structure and thus the electrochemical activity of the fuel electrode [29, 124].

On the other hand, seawater cell 1_{new} exhibits an increase in the resistances R_{RQ1} and R_{RQ2} , where R_{RQ2} is the dominant contribution. In addition, a rapid increase in operation voltage is observed between 400 and 600 hours primarily driven by a rise in R_{RQ2} . In seawater cell 1_{new} Si contamination is found in the Ni-YSZ fuel electrode. The above post test characterization revealed Si contamination in the active layer of the Ni-YSZ fuel electrode blocking active sites and poisoning the electrode. This leads to an increase in the operational voltage and the resistance connected to the electrochemical reaction [27, 33, 89]. Interestingly, unlike pure water cell 4_{new}, no densification of the Zr phase is observed in seawater cell 1_{new}. This raises the question of whether seawater utilization suppresses the densification of the Zr containing YSZ phase in the Ni-YSZ fuel electrode.

As CaO and Na species were identified by post test characterization on or within the Ni-YSZ fuel electrode during seawater operation, these are potential candidates that could be able to suppress the densification of the YSZ phase in the Ni-YSZ electrode. There are some hints in literature that this could be a feasible explanation: (1) A study on Ni-YSZ-MO (M = Ca, Mg) suggested that a small addition of these MO oxides could arrest degradation [164]; (2) another study reported that doping of Ni-YSZ fuel electrodes with stable oxides (CaO, MgO) significantly reduced the reoxidation kinetics of Ni based fuel electrodes [165]; (3) it was reported that the use of Ni-YSZ modified with CaO is more stable against carbon deposition, however, decreased the performance [166]; (4) a recent study reported increased stability against low temperature hydrothermal degradation of CaO doped 3-YSZ in comparison to pure 3-YSZ [167]. In conclusion, literature reported that a stable backbone structure of YSZ in the Ni-YSZ fuel electrode can effectively mitigate degradation [168-169]. Given the absence of Zr phase densification during seawater operation and the identification of CaO deposits, it is possible that CaO contributes to stabilizing the YSZ phase under the chosen operating conditions. This phenomenon must be investigated in future studies to validate the hypothesis by the author based on the reported results here.

In summary, the electrochemical results demonstrate that the direct utilization of seawater does affect the stability of SOECs operated in steam electrolysis conditions over 1000 hours of operation. This finding contrasts with previous studies on seawater operation which reported negligible degradation effects^[9, 14-15, 94]. This difference is attributed to a more detailed and precise comparison to pure water operation and the extended operation times employed in this thesis. The higher degradation rates observed during seawater operation are primarily linked to Si poisoning in the Ni-YSZ fuel electrode, confirmed by post test characterization. Si is known to be present in seawater as an impurity^[14]. Furthermore, from post test characterization, the transport of salt impurities to the SOEC during operation was confirmed which contradicts current publications on seawater operation in SOECs^[9, 14-15, 94]. Moreover, in pure water operation a densification of the Zr phase in the active layer of the Ni-YSZ fuel electrode mainly led to the seen degradation. This densification is not present in seawater operation. From literature analysis it is suggested by the author that the transport of CaO to the cell is beneficial for suppressing Zr phase densification in the Ni-YSZ fuel electrode, potentially mitigating related degradation.

6.3 Direct Saturated Sodium Chloride Solution Utilization

In the next chapter, a concentrated sodium solution is investigated for its direct use in steam production for SOEC single cells. As shown in the previous chapter, the utilization of seawater impacts the stability of a SOEC over 1000 hours of operation time, primarily due to Si poisoning. However, the reported transport of salts (see chapter 6.2) to the cell could influence the long term durability of SOECs negatively over the expected and needed lifetime of approximately 10 to 15 years. Thus, testing of concentrated salt solutions as an accelerated stress test could give insights as more salt particles as aerosols are transported to the cell. Furthermore, high salinity wastewater is commonly found in several industrial processes and their direct use in SOECs could represent an innovative approach to wastewater utilization.

In this chapter, saturated sodium chloride (NaCl) solution is used as NaCl is the dominant salt in seawater and is also present in industrial wastewaters such as those from polycarbonate production. Thus, the following experiments aim to evaluate the use of high salinity wastewater from industry directly in SOEC systems while simulating accelerated stress testing for seawater operation. The author wants to note here that for the stability test two cells of the old cell batch are compared. As discussed in chapter 6.1 the old production batch shows Si poisoning due to material impurities. The used sodium chloride solution is produced by dissolving of NaCl salt in ultrapure water that is also used for the pure water test. Therefore, no Si transport to the cell during operation is expected.

The initial performance and the ASR are evaluated by iV curve measurements and compared to results obtained using steam generated from pure water. The long term stability is assessed

by a stability test over 1000 hours, supported by electrochemical measurements including iV curves and EIS measurements and analysis. Finally, the degraded cell is post characterized to identify transported impurities and to evaluate degradation mechanisms occurring during operation. XPS surface analysis of the Ni-YSZ fuel electrode was performed by ZEA-1 at Forschungszentrum Jülich. The Ni-YSZ fuel electrode surface and polished cross section SEM-EDX measurements were recorded in cooperation with Jean Pierre Puc and Pritam Chakraborty from Dr. Basak's group. Selected results presented in this chapter are published in ^[114].

6.3.1 Electrochemical Initial Performance

The initial electrochemical performance of a cell operated with steam generated from saturated sodium chloride (NaCl) solution was evaluated as a function of operation temperature. Figure 40a displays the respective iV characteristics in a temperature range from 750 to 900 °C using a gas composition of 60 % H₂O + 40 % H₂ at the fuel electrode. As predicted by the Nernst equation, the OCV increases with decreasing temperature. The theoretically calculated OCVs using the Nernst equation and experimental measured OCVs are shown in Table A 12 in the appendix. The experimentally determined OCVs deviate up to 2 % from the theoretical calculated values. Deviations from the theoretical OCV are attributed to minor gas leakages between the air and fuel electrode sides ^[90]. As expected, the electrochemical performance decreases with a decrease in temperature due to lower kinetics and higher electrochemical process and ohmic resistances. The curvature of the iV characteristics at high temperatures and high current density is attributed to transport limitations.

To evaluate the influence of steam content, additional iV curves were recorded. Figure 40b shows the iV characteristics at a constant temperature of 800°C and different steam contents for a cell operated with saturated NaCl solution. Hydrogen was used as balance gas. The respective theoretical and experimentally observed OCV values are summarized in Table A 13 in the appendix. As with the temperature variation, differences of up to 1 % between theoretical and experimental determined OCVs are observed and explained by minor gas leakages in the setup ^[90]. The highest performance in SOEC mode is reached with the highest steam content of 60 %. With a decrease in steam content, the performance is decreasing.

Figure 40c compares the current densities at 1.4V with 60 % H₂O content for the NaCl saturated solution with those obtained using steam from pure water at different temperatures. The measured current densities are similar in both cells, indicating no negative impact when using NaCl saturated solution for steam production in SOEC operation. As described in chapter 6.2, the activation energy is calculated from the ASR values, derived from the slope of the iV curves at OCV and at a current density of $-0.5 \text{ A} \cdot \text{cm}^{-2}$ in electrolysis mode using a model that

includes a thermally activated electrochemical contribution and a temperature independent gas transport related contribution, as introduced (see chapter 6.2.1.3).

The resulting Arrhenius plots of the ASR for a cell operated with a saturated NaCl solution are shown in Figure 40d. The fitted gas concentration related resistance R_{diff} is $0.099 \Omega \cdot \text{cm}^2$ at OCV and $0.084 \Omega \cdot \text{cm}^2$ at $-0.5 \text{ A} \cdot \text{cm}^{-2}$, respectively. These values are in the same range as those observed for cells operated with pure water and seawater discussed in chapter 6.2.1.3. Therefore, the R_{diff} seems not influenced by the operation of the cell with saturated NaCl solution.

The fitted activation energies refer to $117 \text{ kJ} \cdot \text{mol}^{-1}$ and $115 \text{ kJ} \cdot \text{mol}^{-1}$ at OCV and $-0.5 \text{ A} \cdot \text{cm}^{-2}$ which are consistent with values obtained for pure water and seawater operation (see chapter 6.2.1.3). In conclusion, no significant or negative influence on the initial performance is observed for the operation of a SOEC with saturated NaCl solution, indicating the feasibility of using high salinity water sources in SOEC systems.

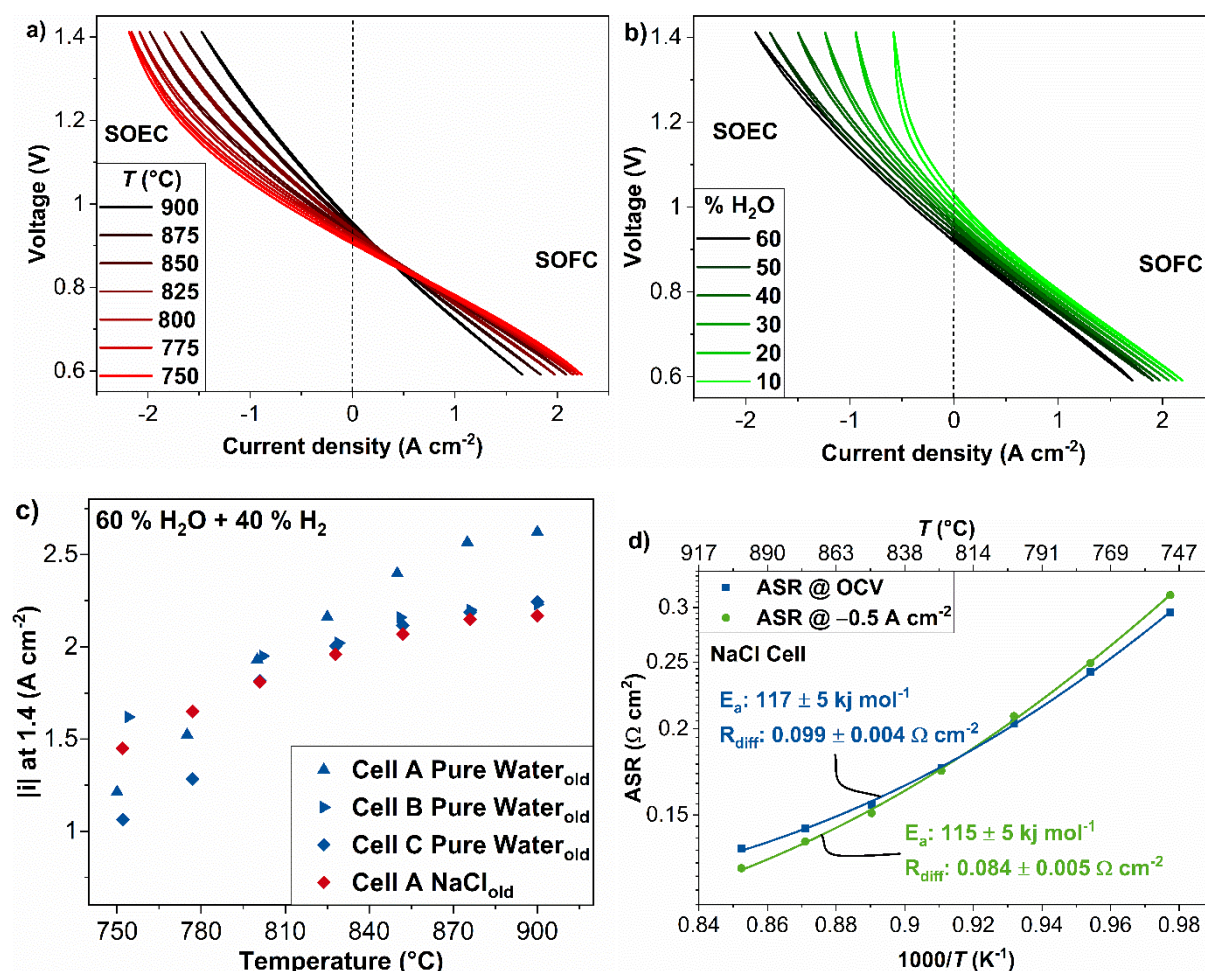


Figure 40 iV curves recorded at (a) different temperatures and constant gas compositions of 60 % H_2O + 40 % H_2 at the fuel electrode and (b) at different steam contents and a constant temperature of 800 °C. (c) Current densities at 1.4 V at 800 °C and 60 % H_2O + 40 % H_2 in comparison with pure water reference measurements. (d) Evaluation of the activation energy of the NaCl operated cell.

6.3.2 Long Term Stability Test

6.3.2.1 Operation Voltage Evolution

Figure 41a presents the voltage time curves for a cell operated with steam generated from a saturated sodium chloride solution (NaCl cell 1_{old}) and a reference cell operated with pure water (pure water cell 3_{old}). Both investigated cells originate from the older production batch which showed Si poisoning in their initial materials (see chapter 6.1). The concentrated sodium chloride solution used for the NaCl cell was prepared by dissolving NaCl in ultrapure water from the same source as the water used in the pure water cell. Therefore, no additional Si transport to the cell during operation is expected. The stability test was performed under galvanostatic operation with $-1 \text{ A}\cdot\text{cm}^{-2}$ current load at 800°C and a gas composition of 60 % H_2O + 40 % H_2 .

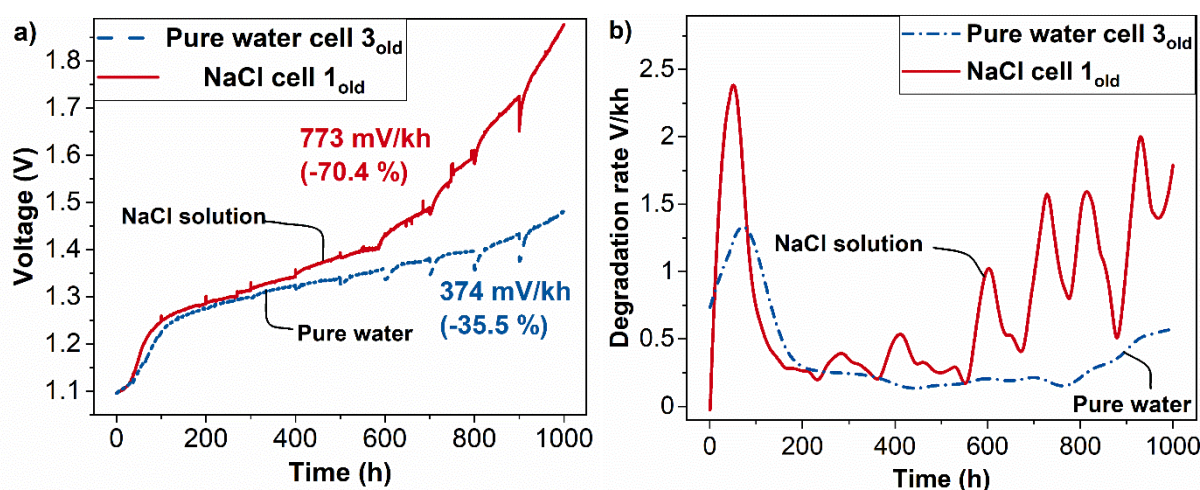


Figure 41 (a) Voltage and (b) degradation rate evolution over time for cells operated with steam generated from saturated NaCl solution (red) and pure water (blue) at a constant current density of $-1 \text{ A}\cdot\text{cm}^{-2}$, a temperature of 800°C and a gas composition of 60 % H_2 + 40 % H_2O .

NaCl cell 1_{old} exhibits a high degradation rate of $773 \text{ mV}\cdot\text{kh}^{-1}$ over 1000 hours of operation. Pure water cell 3_{old} shows a significantly lower degradation rate of $374 \text{ mV}\cdot\text{kh}^{-1}$. Moreover, pure water cell 3_{old} and NaCl cell 1_{old} both display similar initial starting voltages and voltage evolutions during the first 400 hours of operation. In particular, a steep voltage increase is observed in the first 150 hours of operation as expected for the older cell batch (see chapter 6.1). After 150 to 400 hours both cells exhibit a similar degradation rate and the voltage increases linearly.

After 400 hours of operation, the behavior of the two cells diverges significantly. While NaCl cell 1_{old} exhibits an exponential voltage increase after 400 hours, pure water cell 3_{old} continues to degrade in a linear fashion with a steady rise in cell voltage until 800 hours of operation. After 800 hours until 1000 hours, a slight accelerated voltage increase is visible in pure water

cell 3_{old}. This trend becomes clearer when the evolution of the degradation rate is plotted as a function of the operation time, as shown in Figure 41b for both cells. After 400 hours of operation, the degradation rate of NaCl cell 1_{old} rapidly surpasses that of pure water cell 3_{old}. Table 8 summarizes the absolute degradation rates for every 100 hours in both cells. In the first 100 hours of operation, degradation rates over 1000 mV·kh⁻¹ are observed in both cells. After, lower degradation rates around 250 mV·kh⁻¹ are measured until 400 hours of operation. The degradation rates increase after 400 hours to values over 1000 mV·kh⁻¹ in the time frame from 700 to 1000 hours for the NaCl cell 1_{old}. Pure water cell 3_{old} stays from 100 to 1000 hours of operation under a degradation rate of 600 mV·kh⁻¹.

In summary, the results indicate that operation with NaCl solution leads to accelerated degradation after approximately 400 hours of operation. This points to a time dependent degradation mechanism which could be linked to salt transport or accumulation processes.

Table 8 Degradation rate in absolute numbers every 100 hours of operation time for the utilization of saturated NaCl solution compared to pure water operation.

Degradation time (h)	Degradation rate (mV·kh ⁻¹)	
	Pure Water cell 3 _{old}	NaCl cell 1 _{old}
0 - 100	1120	1483
100 - 200	612	380
200 - 300	259	280
300 - 400	217	300
400 - 500	145	420
500 - 600	178	490
600 - 700	200	540
700 - 800	179	1220
800 - 900	311	1150
900 - 1000	528	1510

6.3.2.2 Current Density Voltage Curves

For a more detailed understanding, the iV curves recorded every 100 hours during the stability test for pure water cell 3_{old} and NaCl cell 1_{old} are shown in Figure 42a and Figure 42b, respectively.

The initial performance of both cells is identical reaching $-2.33 \text{ A}\cdot\text{cm}^{-2}$ at 1.4 V, indicating comparable starting conditions. The current densities decrease continuously over the operation time in both cells. The largest absolute drop in performance occurs within the first 100 hours and reflects the high initial degradation rates. For instance, after 100 hours of

operation, the current density decreases to -1.57 at 1.4 V in NaCl cell 1_{old} and to and -1.79 A·cm⁻² at 1.4 V in pure water cell 3_{old}, respectively.

At 1000 hours the current densities at 1.4 V further decrease to -0.41 and -0.67 A·cm⁻² at 1.4 V for the NaCl and pure water operated cell. In relative numbers, the performance of the NaCl cell 1_{old} at 1.4 V decreased by 82 % over 1000 hours of operation and the performance of the pure water cell 3_{old} by 71 % which is similar to values reported by our group for pure water operation before ^[122]. In addition, both cells exhibit hysteresis of the iV curves after the first 100 hours of the degradation test. As said in the previous chapters, the origin of hysteresis is still under discussion in literature and more detailed information can be found in ^[17, 31, 127-129].

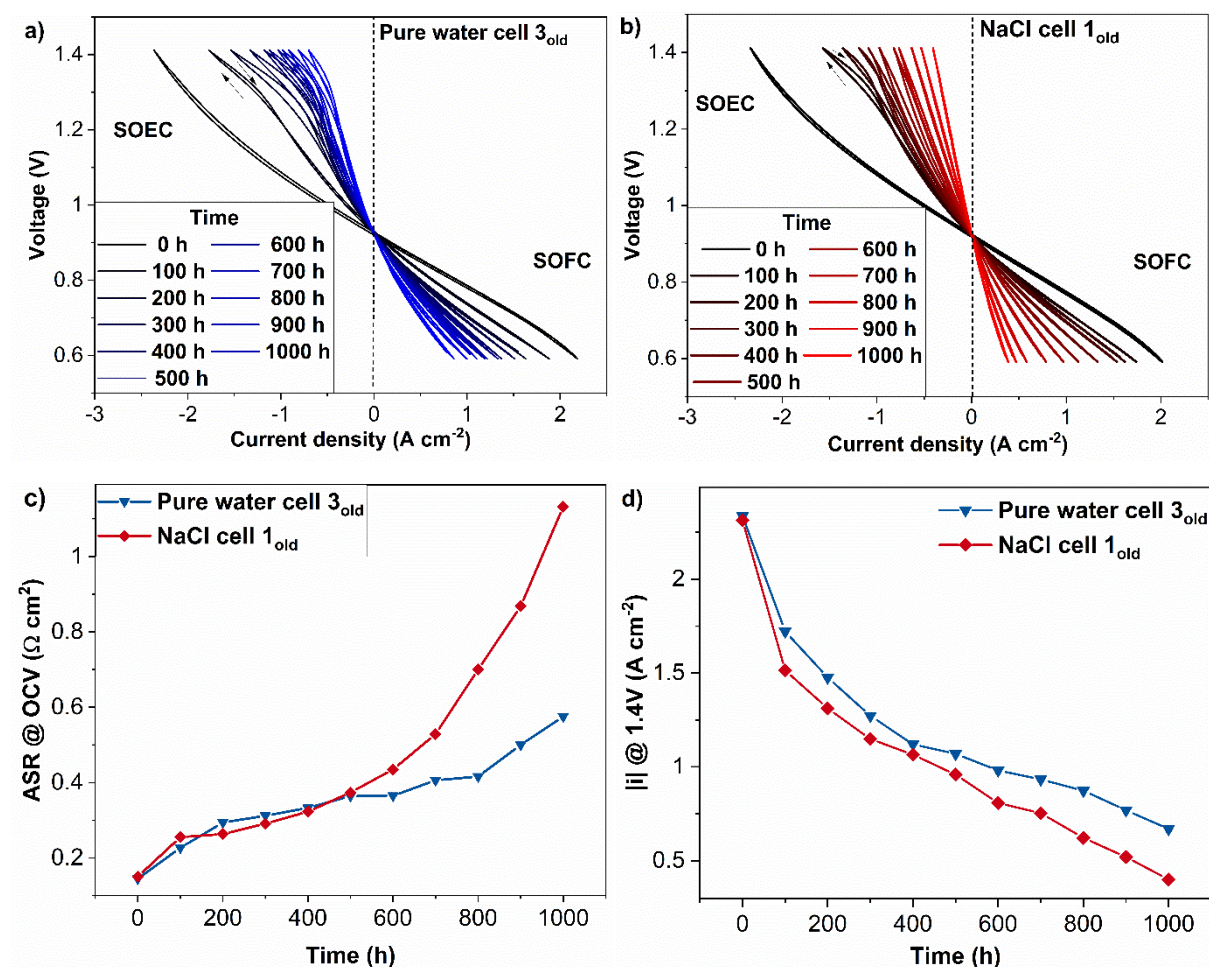


Figure 42 iV curves recorded every 100 hours of operation for (a) pure water cell 3_{old} and (b) NaCl cell 1_{old} during the stability test and the corresponding evolution of (c) the ASR at OCV and (d) the current density at 1.4 V.

Figure 42c presents the evolution of the ASR at OCV as a function of operation time for both the NaCl cell 1_{old} and pure water cell 3_{old}. Initially, both cells exhibit comparable ASR values with values of 145 Ω·cm⁻². In the first 200 hours, a rapid increase in ASR is observed for both cells. Pure water cell 3_{old} demonstrates a linear increase in ASR reaching 0.61 Ω·cm⁻² after

1000 hours of operation. In contrast, the NaCl operated cell exhibits an exponential increase in ASR from 200 to 1000 hours reaching a maximum of $1.13 \Omega \cdot \text{cm}^{-2}$ by the end of the stability test.

Correspondingly, Figure 42d shows the current density at 1.4 V as a function of operation time for both cells. Throughout the entire operation period, it is observed that NaCl cell 1_{old} maintains a lower current density compared to the pure water operated cell. Furthermore, the performance gap between both cells is widening after 600 hours of operation. This is in accordance with the trends observed for both the ASR evolution at OCV and the operation voltage at constant current density of $-1 \text{ A} \cdot \text{cm}^{-2}$, indicating more severe degradation in the NaCl operated cell over time.

6.2.2.3 Electrochemical Impedance Spectroscopy

For a detailed analysis of the accelerated degradation behavior of NaCl cell 1_{old}, the EIS measurements performed at 100 hour intervals during the stability test are analyzed in detail. The corresponding Nyquist plots for NaCl operated cell 1_{old} and pure water operated cell 3_{old} are shown in Figure 43a and Figure 43b, respectively.

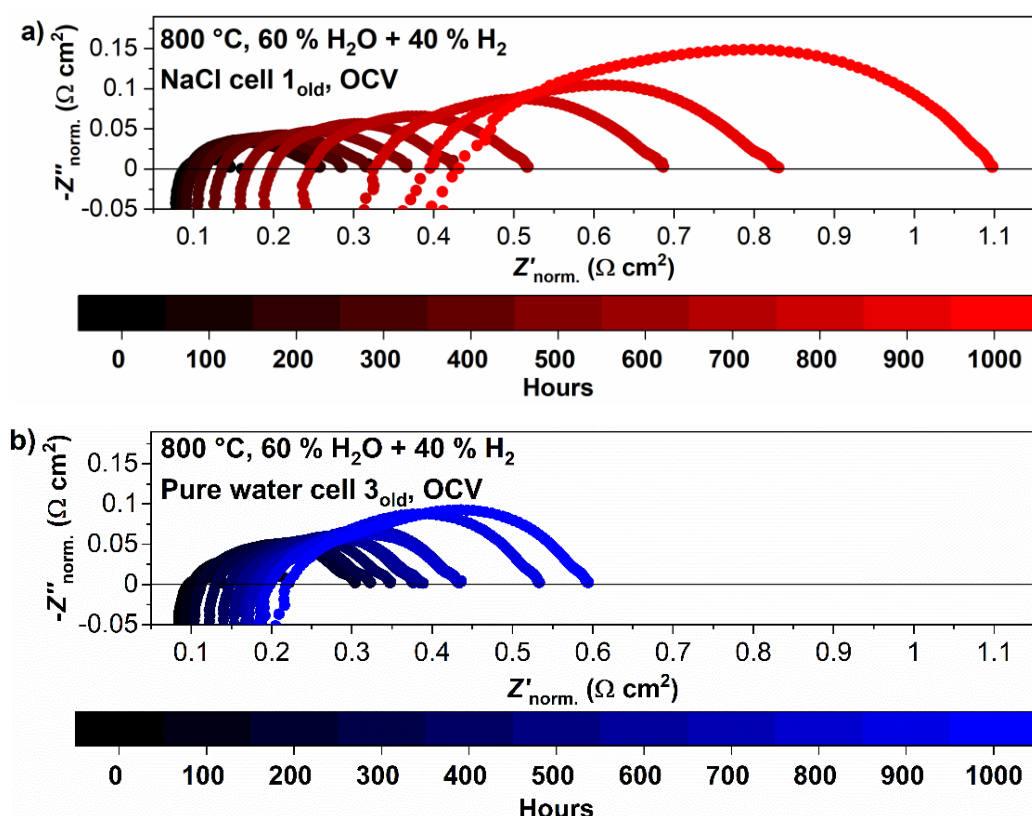


Figure 43 Nyquist plots as a function of operation time for the (a) NaCl cell 1_{old} and (b) the pure water cell 3_{old}.

For NaCl cell 1_{old}, the high frequency intercept with the real impedance axis remains relatively unchanged during the first 200 hours of operation. After 200 hours a gradual increase in the

high frequency intercept is observed. A similar trend is present in pure water cell 3_{old}, however, less pronounced. As discussed in chapters 6.1 and 6.2, a direct interpretation of the high frequency intercept is challenging due to the parasitic inductive effects inherent in both cells. In contrast, the low frequency intercept with the real impedance axis which primarily reflects the polarization resistance, increases throughout the entire operation period in both cells. Notably, a sharp increase after the first 100 hours of operation in the low frequency intercept is seen in both cells. This increase is more pronounced after 600 hours of operation in NaCl cell 1_{old} compared to pure water operating indicating a correlation with the accelerated degradation during NaCl operation.

For a more detailed analysis and a deconvolution of the EIS data, the data is fitted by an ECM. The ECM consists of an inductance in series with a resistor and four RQ elements, each representing distinct electrochemical processes in the cell, as described in detail in chapter 6.1.

Figure 44 illustrates the ohmic resistance and polarization resistance derived from the ECM fitting as a function of operation time for both the NaCl cell 1_{old} and pure water cell 3_{old}. In NaCl cell 1_{old}, R_p increases from $0.073 \Omega \cdot \text{cm}^2$ to $0.180 \Omega \cdot \text{cm}^2$ in the first 200 hours, while R_Ω rises from $0.078 \Omega \cdot \text{cm}^2$ to $0.086 \Omega \cdot \text{cm}^2$. After this period, R_p and R_Ω steadily increase in an exponential manner, with R_p consistently exceeding R_Ω throughout the entire operation. Especially after 600 hours until 1000 hours of operation a sharp increase in R_p is observed leading to a total increase by $0.525 \Omega \cdot \text{cm}^2$ in this period. After 1000 hours R_Ω reaches a value of $0.334 \Omega \cdot \text{cm}^2$ and R_p a value of $0.788 \Omega \cdot \text{cm}^2$.

In contrast, pure water cell 3_{old} exhibits a more moderate increase in resistances. During the first 200 hours, R_p increases from $0.066 \Omega \cdot \text{cm}^2$ to $0.213 \Omega \cdot \text{cm}^2$ and R_Ω from $0.080 \Omega \cdot \text{cm}^2$ to $0.096 \Omega \cdot \text{cm}^2$. Between 200 hours and 600 hours of operation, R_p remains approximately constant, and R_Ω increases to a value of $0.160 \Omega \cdot \text{cm}^2$. From 600 to 1000 hours, R_Ω stays stable and R_p increases from $0.235 \Omega \cdot \text{cm}^2$ to $0.450 \Omega \cdot \text{cm}^2$.

The sharp voltage increase observed during the initial 200 hours of operation in both cells is primarily attributed to a rise in R_p , consistent with the previous discussion in chapter 6.1.

However, the accelerated degradation in NaCl cell 1_{old} after 600 hours is due to an accelerated increase in R_p and R_Ω after 600 hours. In addition, R_p is the dominant contribution to the more pronounced degradation.

For a more detailed analysis of the degradation behavior, the evolution of the individual resistances associated with each RQ element in the ECM is presented in Figure 45a and Figure 45b for NaCl cell 1_{old} and pure water cell 3_{old}, respectively.

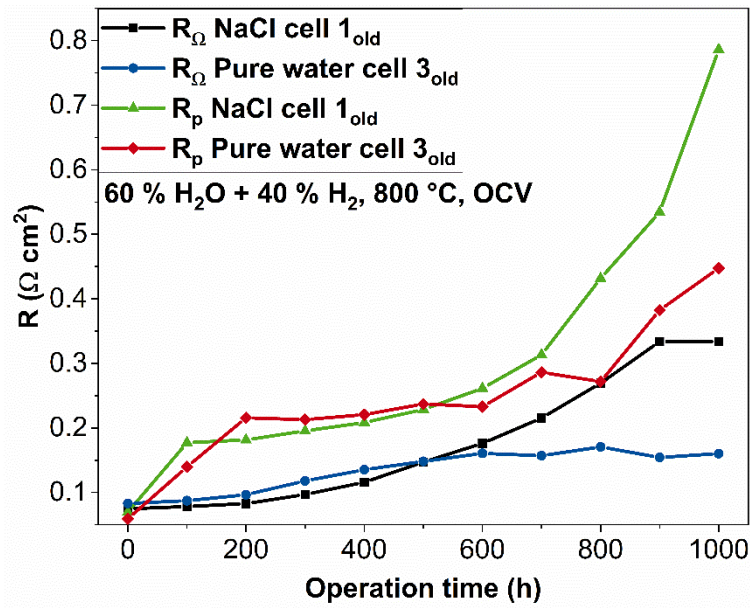


Figure 44 Evolution of the ohmic and polarization resistance during the stability test comparing the utilization of steam produced from pure water and NaCl solution. The values are derived from the EIS measurements in a gas composition of 60 % H₂O + 40 % H₂ at 800 °C and OCV.

The resistance R_{RQ4} appearing at low frequencies remains unchanged over the entire operation period for both cells. Similar, R_{RQ3} shows a slight increase over the operation period in both cells, however, does not contribute significantly to the rise in R_p discussed above. In contrast, the resistance R_{RQ2} exhibits a sharp increase in the first 200 hours of operation in both cells followed by a steady increase until the end of the operation. However, this steady increase is more pronounced in NaCl cell 1_{old} compared to pure water operation.

The resistance R_{RQ1} increases in the first 200 hours in both cells and remains stable between 200 and 400 hours. After 400 hours until 600 hours, R_{RQ1} shows a gradual increase in the case of the NaCl cell 1_{old}, whereas it remains nearly constant in pure water cell 3_{old}. After 600 hours of operation, R_{RQ1} increases sharply until the end of the measurement in both cells. However, the increase is more pronounced in the case of the NaCl cell 1_{old} even surpassing the resistance R_{RQ2} which is not observed in pure water cell 3_{old}.

The observed rapid increase in voltage during the first 200 hours in both cells is primarily due to an increase in R_{RQ2} , while the voltage acceleration after 600 hours is dominated by the growth of R_{RQ1} . R_{RQ3} and R_{RQ4} do not significantly contribute to the degradation of the polarization resistance. The accelerated increase in voltage and R_p after 600 hours of operation in NaCl cell 1_{old} is mainly related to an accelerated increase in R_{RQ1} , whereas R_{RQ2} is increasing more pronounced as well.

These trends are further corroborated by the evolution of the distribution of relaxation times (DRT) analysis shown in Figure 45c and Figure 45d for the NaCl cell 1_{old} and pure water cell 3_{old}, respectively.

The low frequency peak P_5 remains unchanged in both magnitude and relaxation frequency across the test duration in both cells. The low to intermediate frequency peaks P_4 and P_3 slightly increase in magnitude and shift to lower relaxation times with an increase in operation time. In NaCl cell 1_{old}, P_3 shows a more substantial rise in magnitude compared to pure water operation. P_2 exhibits a clear increase in magnitude and a shift to lower relaxation frequencies in both cells. In the case of NaCl cell 1_{old}, the increase in P_2 is more pronounced compared with pure water cell 3_{old}.

The high frequency peak P_1 increases in magnitude with time while its relaxation frequency remains constant in both cells. Again, the increase in the magnitude of P_1 is more pronounced in NaCl cell 1_{new} compared to pure water operation.

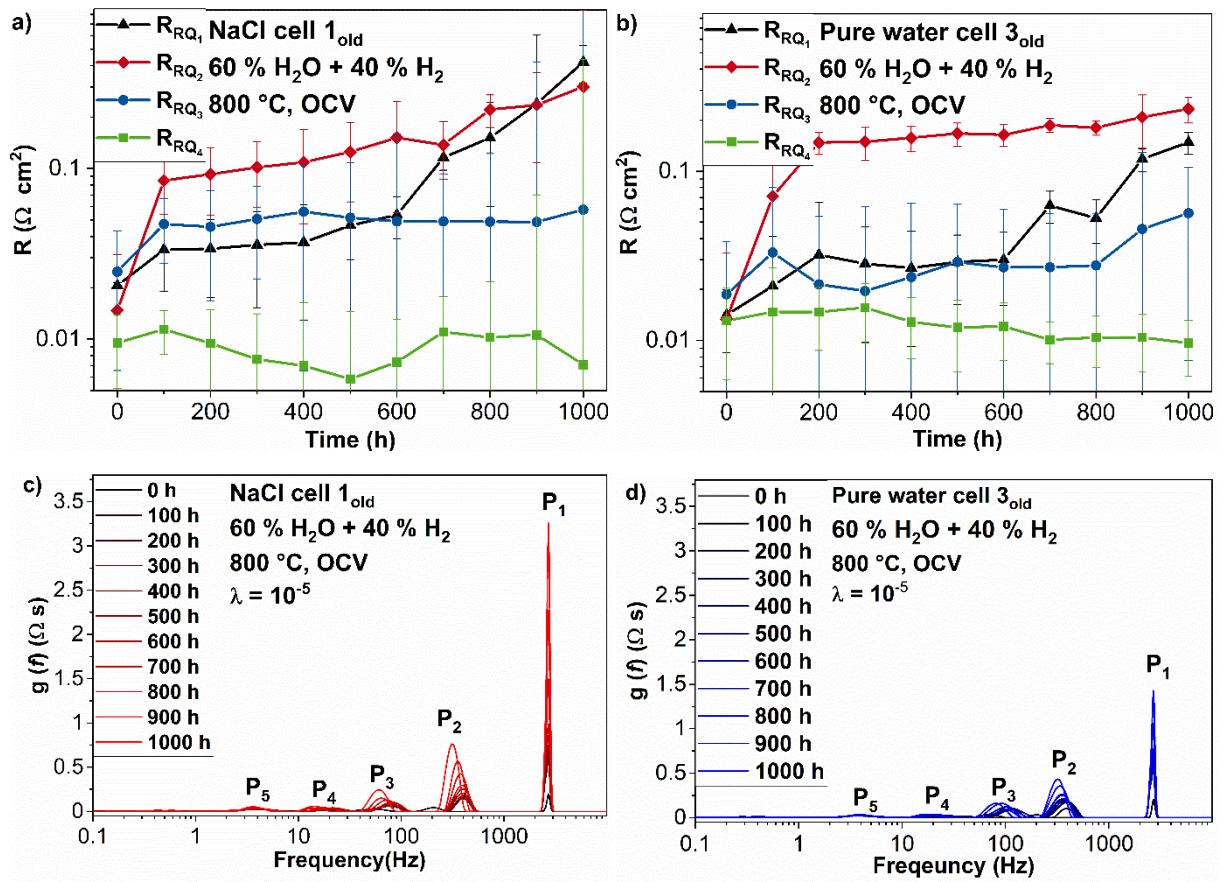


Figure 45 Individual resistance analysis derived from ECM fitting for the (a) NaCl cell 1_{old} and the (b) pure water cell 3_{old}. Corresponding DRT plots as a function of operation time for (c) the NaCl cell 1_{old} and (d) the pure water cell 3_{old}. Data is derived from EIS measurements at 800 °C and OCV with a gas composition of 60 % H₂O + 40 % H₂ conducted every 100 hours of operation.

From the DRT analysis, it is evident that the high frequency peaks P_1 and P_2 are the dominant contributors to the increase in R_p in both cells. Therefore, these processes are the major drivers for the accelerated degradation observed in the NaCl cell 1_{old} compared to pure water cell 3_{old}, consistent with the ECM based findings.

As established in chapter 3.2.3 the RQ elements and peaks in the DRT are attributed to physical processes. The processes corresponding to R_{RQ1}/P_1 and R_{RQ2}/P_2 are assigned to the electrochemical reaction at the Ni-YSZ fuel electrode [59, 61]. In conclusion, the more pronounced increase in R_p in the NaCl operated cell is caused by degradation mechanisms that affect the electrochemical activity of the Ni-YSZ fuel electrode.

6.3.2.4 Post Test Characterization

The accelerated degradation corresponding to the Ni-YSZ fuel electrode polarization and the ohmic resistance observed and clarified by EIS analysis in the NaCl operated cell was further investigated by post test analysis. This enables a correlation between the electrochemical results and microstructural changes or impurity detection.

Firstly, the surface of the Ni-YSZ fuel electrode was scanned to detect potential salt deposits resulting from impurity transport during operation. Subsequently, the cross section was investigated by SEM-EDX analysis to identify compositional inhomogeneities and microstructural evolution.

In the first step, the surface of the Ni-YSZ fuel electrode was characterized by XRD measurements to identify possible impurities with crystal structures. Figure 46a presents the respective XRD patterns of both cells. Only the expected Ni and YSZ phases are identified, with no additional crystalline phases present. Furthermore, no significant differences between the XRD spectra of NaCl cell 1_{old} and pure water cell 3_{old} are identified, indicating the absence of large scale crystallized salt contaminants.

For enhanced surface sensitivity and the detection of minor crystalline surface species on the Ni-YSZ fuel electrode surface, GI-XRD measurements were conducted. Figure 46b shows the respective GI-XRD spectra for pure water cell 3_{old} and NaCl cell 1_{old}. In both cells, only peaks corresponding to Ni and YSZ are present, like the standard XRD results. The increased Ni to YSZ peak intensity ratio in the GI-XRD is attributed to the thin Ni contact layer which is printed on top of the Ni-YSZ fuel electrode. Furthermore, no salt deposits are detected on the surface of the Ni-YSZ fuel electrode in NaCl cell 1_{old}. These findings suggest that no significant crystallized salt deposits are formed during 1000 hours of operation with steam generated from saturated NaCl solution.

Next, the Ni-YSZ fuel electrode of NaCl cell 1_{old} was characterized by XPS measurements. The corresponding spectrum is shown in Figure 47. As expected, peaks referring to the constituent elements of the Ni-YSZ electrode (Ni, O, Y and Zr) were observed. Additionally, two distinct peaks at binding energies of approximately 1080 eV and 500 eV were detected which are attributed to Na 1s and Na KLL Auger transitions, respectively. These signals confirm the presence of sodium containing deposits on the surface of the Ni-YSZ electrode in NaCl cell 1_{old}. Figure A 6 illustrates a reference XPS spectrum of pure water cell 3_{old} where no sodium

related signals were observed, validating that the observed Na peaks are associated with the operation using saturated NaCl solution.

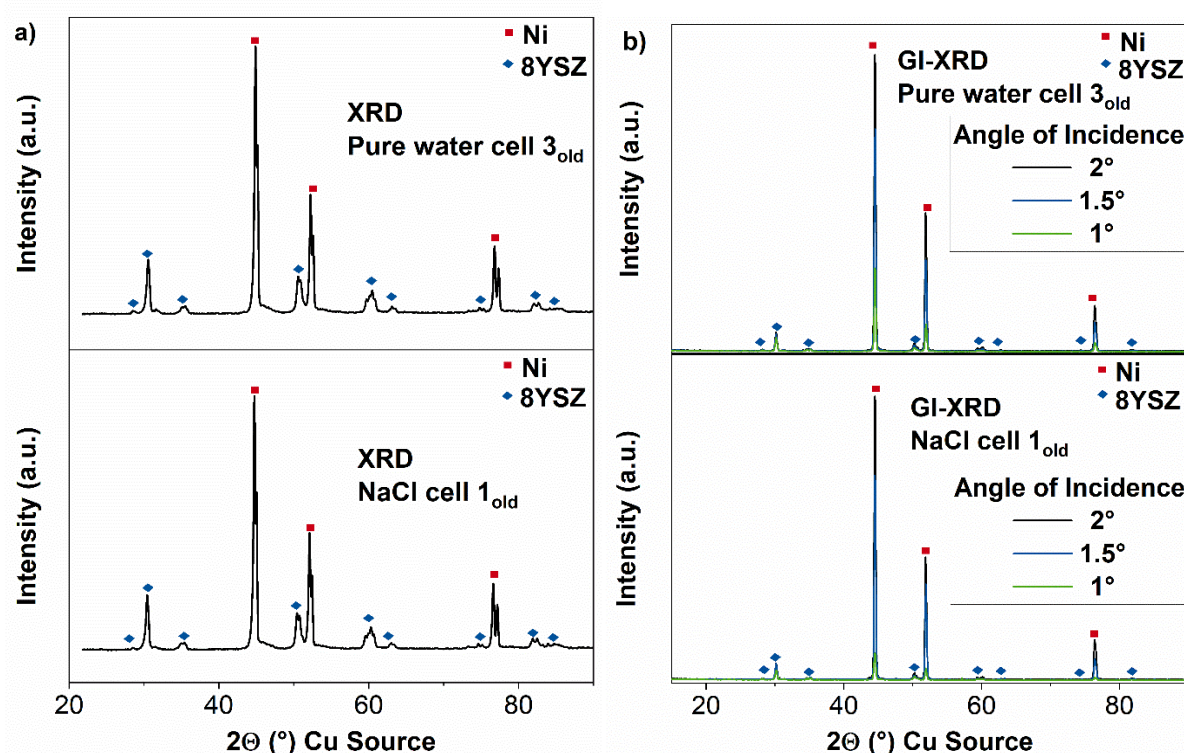


Figure 46 (a) XRD spectra and (b) GI-XRD spectra of the Ni-YSZ fuel electrode surface of pure water cell 3_{oldest} and NaCl cell 1_{oldest}. Both cells were characterized after disassembly out of the measurement setup and exposure to air at room temperature.

Quantitative analysis of the XPS data shows the presence of Na at the Ni-YSZ fuel electrode surface at an amount of 2.4 at.% in NaCl cell 1_{oldest}. In conclusion, the XPS measurement provides direct evidence that a Na species is transported and deposited on the fuel electrode during saturated NaCl solution operation.

After the detection of Na containing deposits on the Ni-YSZ fuel electrode surface in NaCl cell 1_{oldest}, SEM and EDX analysis were performed to evaluate the composition of the Na species and to identify their distribution across the electrode surface. Figure 48 illustrates an exemplary analyzed area of the Ni-YSZ surface in NaCl cell 1_{oldest}. With additional areas provided in Figure A 7 in the appendix. In the secondary electron (SE) images, nanometer scale particles were observed, localized on “islands” formed on top of the Ni contact layer. In the corresponding backscattered electron (BSE) image, these particles appear as black dots, whereas the Ni contact layer is dark gray. This indicates a lower averages atomic number of deposits compared to the contact layer.

EDX analysis confirmed these particles as Na containing deposits. Additionally, oxygen (O) and carbon (C) were detected in the same places as the sodium signals, suggesting a Na

carbonate species such as sodium carbonate or sodium hydrogen carbonate on the Ni-YSZ surface. Importantly, no chlorine (Cl) signal was detected, indicating the absence of chloride containing phases like NaCl on the electrode surface.

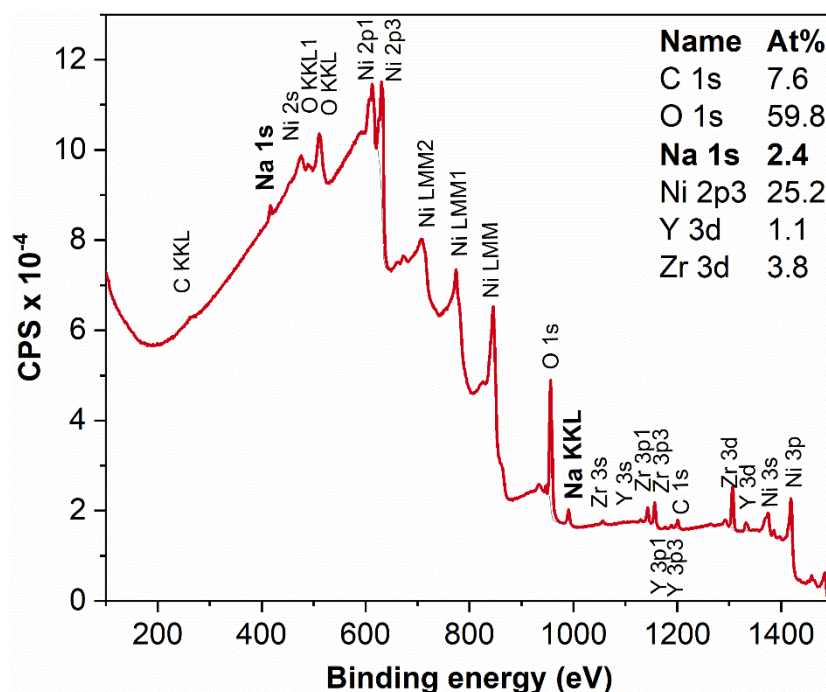


Figure 47 XPS spectrum of the Ni-YSZ fuel electrode surface of NaCl cell 1_{old} at room temperature.

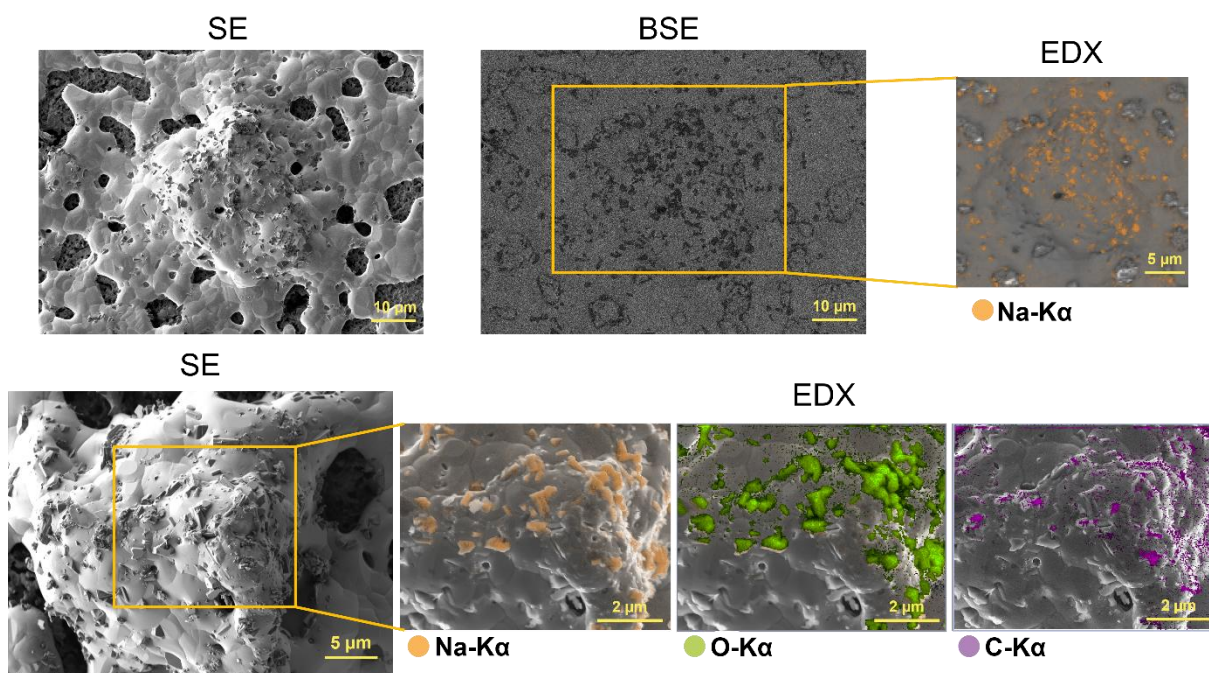


Figure 48 SEM images including SE, BSE and EDX maps of the fuel electrode surface of the NaCl operated cell.

The SEM images show that the distribution of the Na carbonate species was found to be non uniform. The particles are primarily found on localized “islands”, which correspond to topographically elevated features of the Ni contact layer on the fuel electrode. In “flat” regions only minor or no deposits were detected as displayed in Figure A 8 in the appendix. This inhomogeneous distribution suggests that due to a Ni mesh acting as current collector which is attached to the Ni contact layer, only deposits are found in non contacted areas as graphically presented in Figure 49. Considering the localized nature of the Na–carbonate deposits, the author argues that an influence on the electrical contact between the Ni-YSZ fuel electrode and the current collecting Ni mesh is unlikely. Consequently, the accelerated increase in R_{Ω} observed for NaCl cell 1_{old} (as discussed in chapter 6.3.2.3) cannot be attributed to surface deposition of these carbonate species on the Ni-YSZ fuel electrode surface.

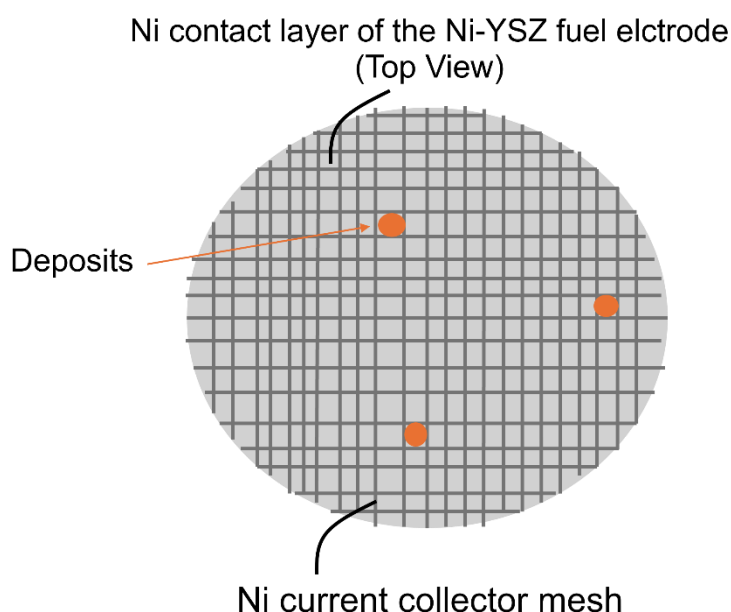


Figure 49 Schematic visualization of the non uniform deposited salt particles on “islands” on the Ni-YSZ fuel electrode surface.

It was previously demonstrated that salt species are transported to the cell during operation and detected on the surface of the Ni-YSZ fuel electrode. Next, the cross section of the Ni-YSZ fuel electrode was analyzed to evaluate the presence of salt related impurities. For this purpose, the cell was fractured and analyzed by SEM-EDX analysis. In the secondary electron (SE) images shown in Figure 50, nanoscale particles are observed covering some grains within the active functional layer near the electrolyte of the Ni-YSZ fuel electrode. As shown earlier in chapter 6.1., identical particles were detected in the reference pure water operated cell (pure water cell 3_{old}), also presented in Figure 50. These particles have been identified as ZrO₂ nanoparticles that are deposited on Ni particles in the cross section as discussed in previous

literature on similarly operated cells ^[126, 133-134]. However, it cannot be excluded that some of the observed particles are related to salt deposits.

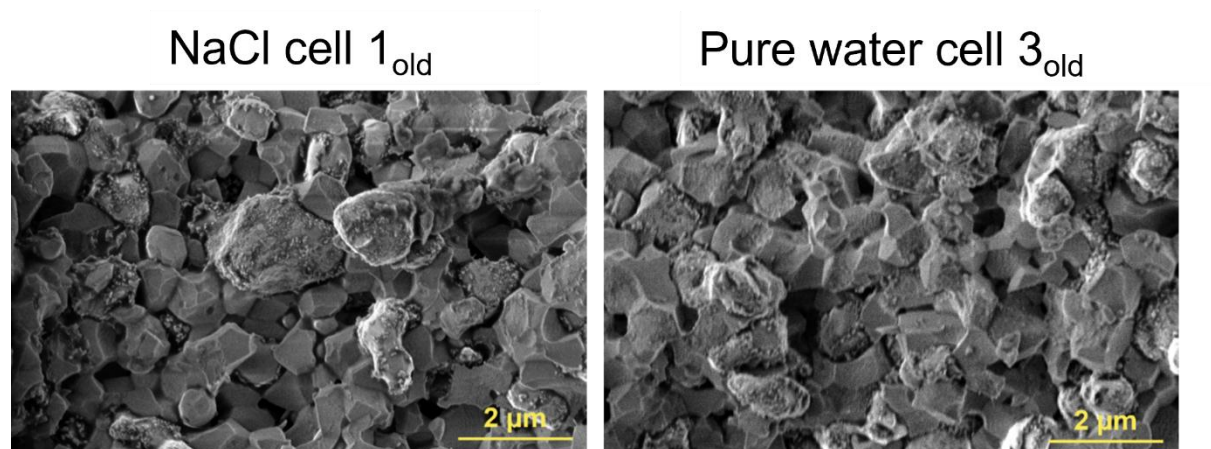


Figure 50 SEM images of the fractured Ni-YSZ fuel electrode AFL of the NaCl operated and pure water operated cell.

Thus, based on SE imaging alone, the identification of salt related impurities in the cross section was not possible. Therefore, EDX analysis was performed on several locations within the fracture cross section of the active layer in the Ni-YSZ fuel electrode of NaCl cell 1_{old}. Data acquisition was challenging due to beam damage. However, the results indicate the presence of Na containing impurities in the Ni-YSZ structure. Figure 51 presents an exemplary EDX spectrum of a spot in the Ni-YSZ fuel electrode of the NaCl cell 1_{old}, revealing a sodium content of 0.33 wt.%. Additional EDX spectra of other locations are presented in Figure A 9 in the appendix, confirming the presence of Na.

No distinct Na containing particles were detected in the EDX mapping, this could be attributed to the spatial resolution of the EDX analysis, which typically ranges from about 10 nm to a few micrometers ^[170]. In addition, the European Network of Forensic Science Institutes states in their guidelines a spatial resolution of a few 100 nm ^[171]. In contrast, on salt transport via bubble bursting in NaCl solutions reports the transport of aerosol particle sizes with a diameter between 10 to 100 nm which could potentially falling below the detection limit of the EDX mapping ^[172].

Interestingly, no chlorine signals were detected in any of the analyzed regions. This is in accordance with the surface analysis of the Ni-YSZ fuel electrode described earlier. Therefore, the results suggest sodium containing species are transported into the Ni-YSZ fuel electrode cross section. Salt deposits could block electrochemical active sites and hinder gas phase diffusion, contributing to the increase in R_p discussed in chapter 6.3.2.3. Additionally, blocking electrochemical sites near the Ni-YSZ/electrolyte interface may contribute to the seen

accelerated increase in R_{Ω} . Over 10 years of operation, salt deposits in the Ni-YSZ fuel electrode could become critical, potentially accelerating cell degradation.

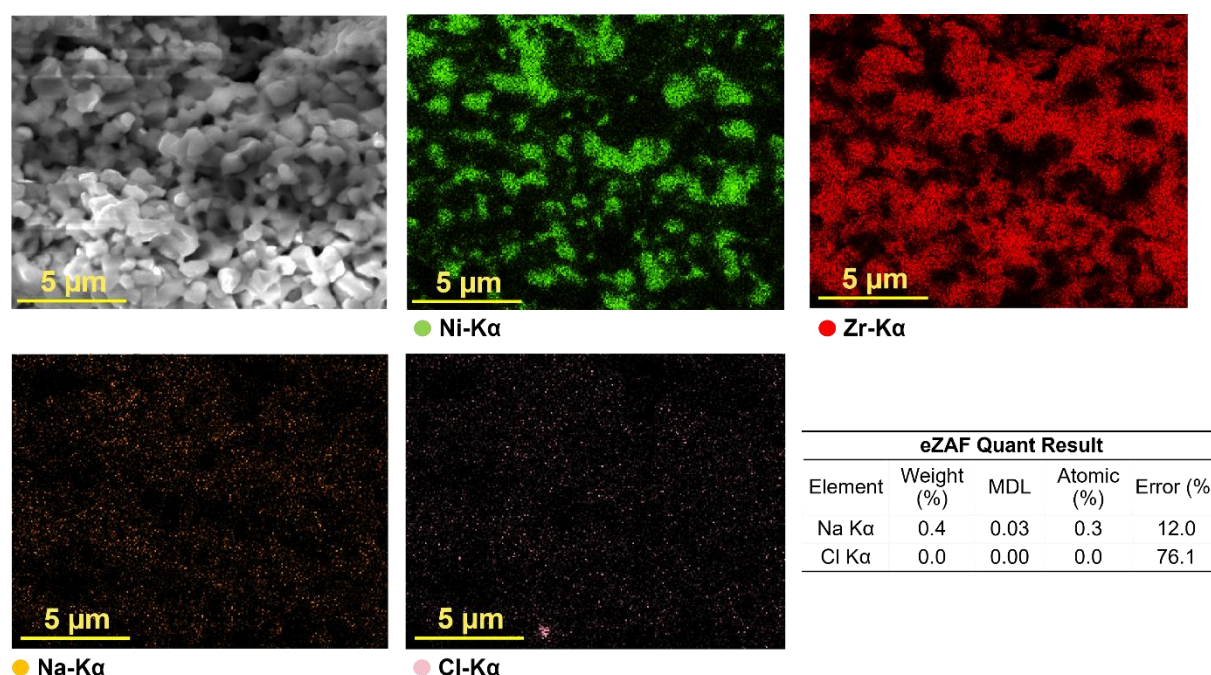


Figure 51 EDX mapping of the fractured Ni-YSZ fuel electrode active function layer of NaCl cell 1_{old}.

Next, the embedded, polished and gold sputtered cross sections of pure water cell 3_{old} and the NaCl cell 1_{old} were analyzed and compared. It should be noted that no delamination of the fuel or air electrode was observed as shown in Figure A 10a in the appendix. Therefore, an accelerated increase in R_{Ω} or R_p by air or fuel electrode delamination is ruled out. In addition, similar microstructures for the polished cross sections of the air electrode were observed for both cells as shown in Figure A 10b in the appendix. Thus, contributions from the air electrode to the overall degradation are unlikely, in accordance with the EIS analysis discussed in chapter 6.3.2.3.

Figure 52a presents SEM images of the Ni-YSZ fuel electrode cross sections of a pristine reduced cell, pure water cell 3_{old} and NaCl cell 1_{old}. In the images, the lighter grey phase corresponds to Ni, while the slightly darker phase corresponds to the YSZ phase. In the pristine reduced cell, the Ni and YSZ phases are well distributed and interconnected within the active function layer of the Ni-YSZ fuel electrode.

In contrast, pure water cell 3_{old} exhibits qualitative signs of Ni particle agglomeration in the active and support layer of the Ni-YSZ fuel electrode. In addition, gaps between the YSZ and Ni phases are apparent in the active functional layer leading to a loss of the well percolating network, as indicated by the red arrows in the SEM image. The black inclusions incorporated

in the Ni particles, indicated by the red squares in the SEM image, were identified as silica species, as discussed in chapter 6.1.

Similar microstructural features are present in NaCl cell 1_{old}. Notably, an increased number of gaps between the Ni and YSZ phases are visible compared to pure water cell 3_{old}, as indicated by the red arrows. Black spots incorporated in the Ni particles are indicated by red squares. The pronounced appearance of gaps between the ionic YSZ and electronic conducting Ni phases could explain the higher increase in R_{Ω} seen in the NaCl operated cell during the long term operation.

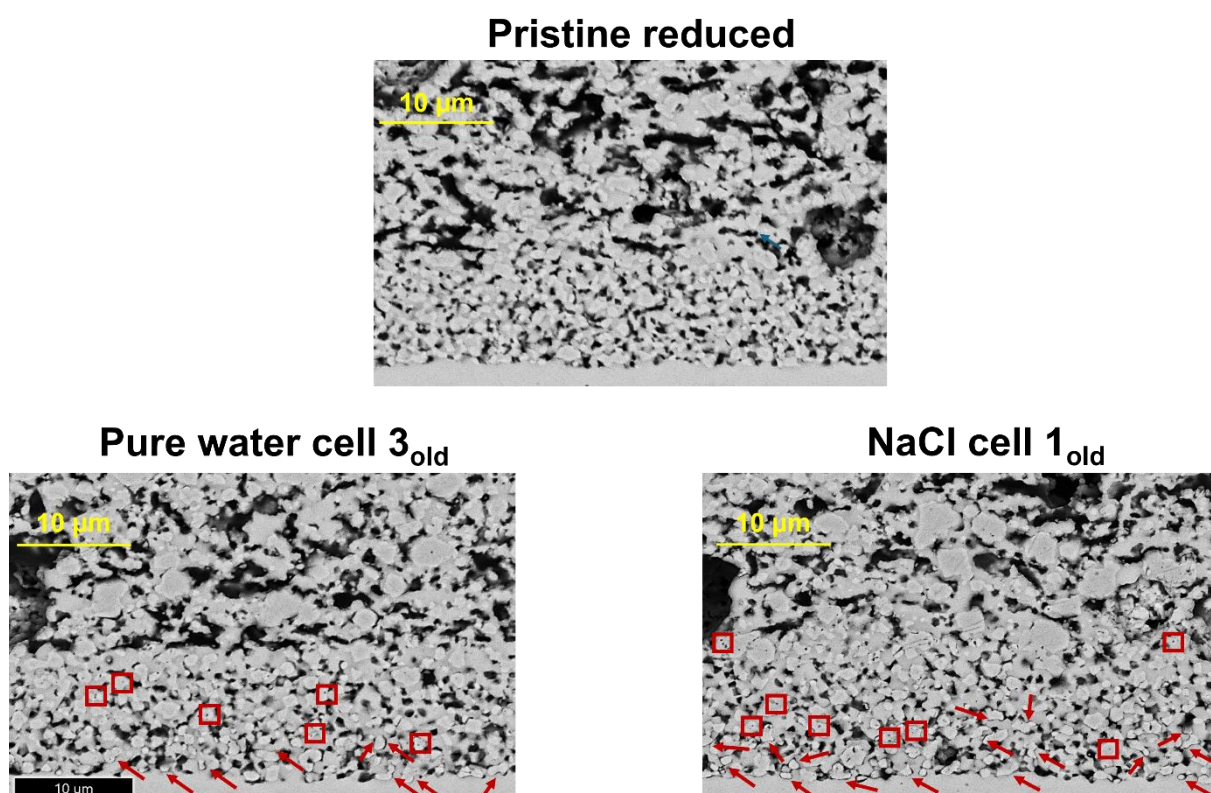


Figure 52 SEM images show the embedded and polished cross section of the Ni-YSZ electrode of a pristine reduced cell, pure water cell 3_{old} and the NaCl cell 1_{old}. Red arrows indicate gaps between the Ni and YSZ phases, while red squares mark inclusions within the Ni particles.

To distinguish better between the Ni and YSZ phases, EDX maps of the cross sections were analyzed, as presented in Figure 53. In the pristine reduced cell, a homogeneous distribution of the Ni phase and the YSZ matrix is observed. Here, fine Ni particles are visible in the active functional layer, while larger Ni particles dominate in the support layer.

In contrast, pure water cell 3_{old} exhibits an agglomeration of Ni particles in both the active functional layer and the support layer of the Ni-YSZ electrode. In addition, Ni is visible in the region approximately 10 μm away from the electrolyte interface, suggesting Ni migration away from the active zone. Thus, bigger Ni particles and lower Ni contents are qualitatively observed

in the active layer of the Ni-YSZ fuel electrode. Furthermore, the YSZ structure appears coarser, indicating microstructural changes in both cells due to the long term operation. In NaCl cell 1_{old}, the most pronounced Ni agglomeration is observed in the active functional and the support layer of the Ni-YSZ fuel electrode. Interestingly, a migration of Ni particles towards the Ni-YSZ fuel electrode/electrolyte interface is evident, opposed to the Ni depletion seen in pure water cell 3_{old}. Moreover, a stronger coarsening of the YSZ structure is visible when compared to the pure water cell 3_{old}, suggesting a higher microstructural degradation.

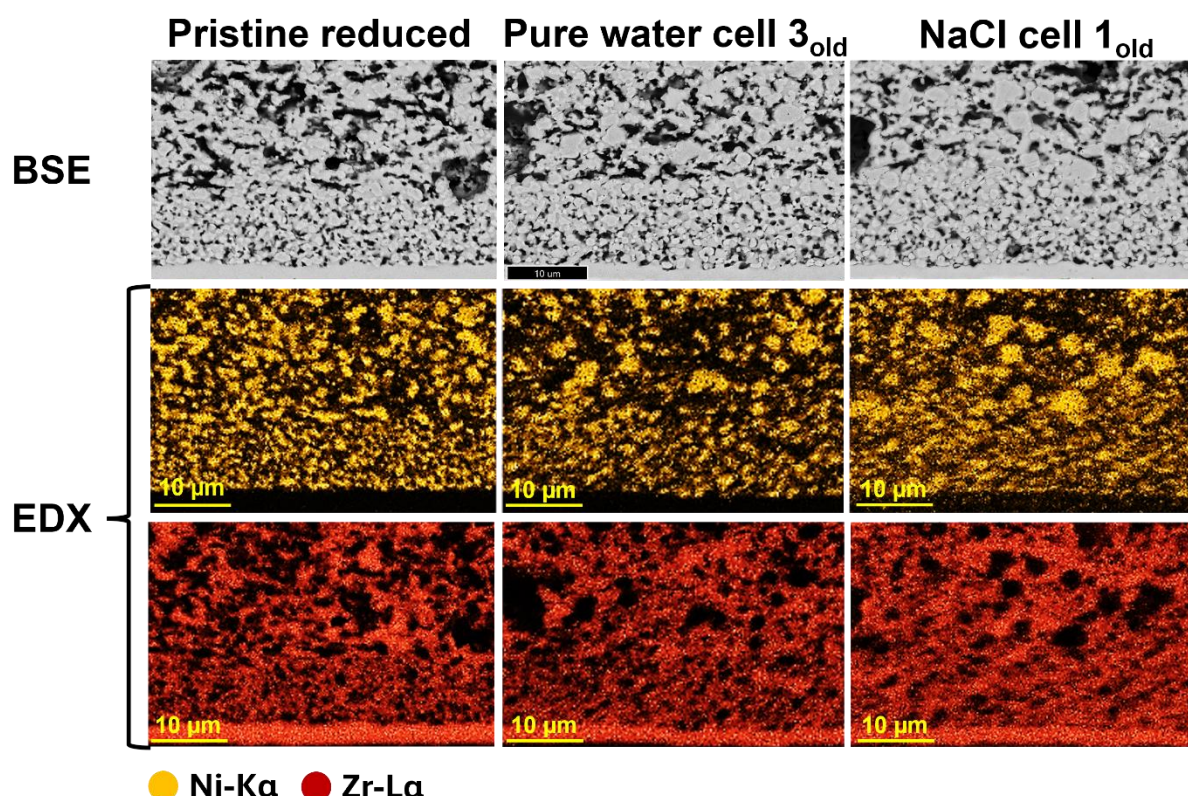


Figure 53 SEM and EDX maps of the Ni and Zr phase of the polished cross section of the Ni-YSZ fuel electrode of a pristine reduced, the NaCl cell 1_{old} and pure water cell 3_{old}.

Table 9 summarizes the quantitative analysis derived from the EDX and SEM image evaluation for both the denser active layer and the porous support layer. NaCl cell 1_{old} exhibits a Ni fraction of 29 % in the active layer of the Ni-YSZ fuel electrode adjacent to the electrolyte, closely matching the 30 % observed in the pristine reduced cell. In comparison, a lower Ni fraction of 26 % is observed in the active layer of the Ni-YSZ electrode in pure water cell 3_{old}. Therefore, in the cell a depletion of Ni away from the electrolyte/electrode interface takes place which is not visible in NaCl cell 1_{old}. In regards of Ni particle sizes, NaCl cell 1_{old} shows higher Ni particle sizes compared to the pristine reduced and pure water cell 3_{old}, particularly within the active layer. Consequently, accelerated Ni agglomeration occurred during operation.

In addition, both cells show an increase in Zr particle size and thus a YSZ phase densification in the active functional layer of the Ni-YSZ fuel electrode after operation, while this is more pronounced in NaCl cell 1_{old} compared to pure water operation.

In summary, these results highlight distinct microstructural evolution pathways in both operated cells. In the case of the pure water cell 3_{old}, a depletion and minor agglomeration of Ni in the active layer is visible. In contrast, for the NaCl cell 3_{old}, a high agglomeration of Ni in the active layer and no depletion of Ni particles is observed. Additionally, more pronounced densification of the Zr phase is visible in NaCl cell 3_{old}.

This raises the question of how transported salt affects the degradation mechanisms and the microstructural evolution. Also, the observation of Na carbonate, rather than NaCl, on the cell surface remains unexplained. In the next paragraph a hypothesis based on the results above is elaborated that seeks to connect the seen salt transport with the differing degradation behavior of NaCl cell 1_{old} compared to pure water operation.

The author wants to reiterate here that the sodium chloride solution used in this chapter was prepared by dissolving NaCl in ultrapure water, the same as used for the pure water tests. Therefore, no additional silicon transport to the cell during operation is expected during operation.

The author proposes that firstly NaCl particles are transported as aerosols to the cell ^[173]. A transported amount of around 15 mg for 1000 hours of operation is calculated based on literature studies using a similar bubbler setup ^[14, 162]. This is in comparison to seawater utilization shown in chapter 6.2 around ten times higher. During SOEC operation, a degradation mechanism increasing the Ni mobility by Ni(OH)_x formation takes place in the Ni-YSZ fuel electrode ^[29]. The presence of NaCl by aerosol transport could facilitate chlorination reactions where Ni(OH)_x reacts with NaCl as chlorination agent to form volatile NiCl_x and NaOH. During the operation at 800 °C, NiCl_x is reduced back to Ni by the hydrogen atmosphere under the formation of HCl ^[174]. The formation of HCl is favored due to its thermodynamic stability under the operation conditions ^[92-93]. Upon exposure to air/oxygen exposure due to the cooling down and assembly of the cell, the NaOH is converted to a sodium carbonate species, as observed on the Ni-YSZ fuel electrode previously presented in the chapter ^[175].

Especially, HCl present in the SOEC could be critical for its long term stability. Prior studies on the effect of HCl contamination on the degradation behavior of SOFC systems revealed an increased degradation due to limitations in the charge transfer at the Ni containing fuel electrode. In addition, another study has shown that trace amounts of HCl (as low as 1 ppm) in the feed gas lead to a sudden increase in voltage after around 400 hours of operation due to a limitation in the charge transfer of the Ni-YSZ fuel electrode ^[32]. This is in accordance with another study, which reported a slight degradation after 300 hours of exposure to HCl, with no

visible degradation during the first 100 hours ^[176]. These studies align with the previously shown electrochemical results presented in chapter 6.3.2.3, where an accelerated increase in polarization resistance was attributed to the degradation of the Ni-YSZ electrode ^[34, 93].

The formation of HCl could also explain the distinct microstructural degradation and the pronounced Ni agglomeration in NaCl cell 1_{old} compared to pure water cell 3_{old}. Chlorine containing species such as adsorbed Cl on Ni surfaces could block active sites in the Ni-YSZ fuel electrode active layer ^[93]. Several studies reported microstructural changes, including the agglomeration or clustering of chlorinated impurities in SOC electrodes due to higher Ni mobility when chlorine contaminations are present in the feedgas ^[176-178]. A higher mobility of the Ni phase either connected to the NiCl_x species or the Ni-Cl_{ads} explains the accelerated agglomeration found in the NaCl operated cell, as discussed in chapter 6.3.2.

Table 9 Quantitative analysis using the SEM and EDX images for the active functional layer and support layer of the Ni-YSZ fuel electrode.

Fraction	Pristine active layer	Pristine support layer	Pure water cell 3 _{old} active layer	Pure water cell 3 _{old} support layer	NaCl cell 1 _{old} active layer	NaCl cell 1 _{old} support layer
Porosity	28 %	39 %	27 %	33 %	28 %	32 %
Ni fraction	30 %	27 %	26 %	23 %	29 %	25 %
Zr fraction	42 %	34 %	47 %	44 %	43 %	43 %
Average						
Ni particle size	0.97 µm	1.09 µm	1.01 µm	1.04 µm	1.11 µm	1.11 µm
Average						
Zr particle size	1.12 µm	1.39 µm	1.23 µm	1.65 µm	1.36 µm	1.67 µm

6.4 Techno Economic Evaluation of Seawater Electrolysis

In this chapter, system level approaches for direct seawater electrolysis in industrial scale SOEC plants are evaluated with respect to their technical and economic risks. This gives insights into the feasibility of seawater electrolysis in SOEC systems and identifies key parameters that must be considered for successful implementation. The technical and economic analysis presented here was conducted in collaboration with the chair of process systems engineering (AVT) at RWTH Aachen as part of the master's thesis of Luca Inkmann in co-supervision with Malte Wernher in the research group of Prof. Matthias Wessling ^[179].

6.4.1 Process Approaches

For the evaluation, the overall process was divided into three main sections: (1) the evaporation section, (2) the SOEC section and (3) the balance of plant (BOP) section. In this thesis, only the evaporation section was varied across different technical configurations, while the SOEC system and BOP components were kept constant for the different cases. As a reference case, a conventional SOEC system using freshwater and a standard evaporator was evaluated. The second case investigated the use of seawater as water source, with a seawater reverse osmosis (SWRO) unit to remove impurities from the seawater, and a conventional evaporator. Additionally, as Si impurities are critical for seawater operation in SOECs (see chapter 6.2) the SWRO unit removes dissolved silica from the seawater ^[180].

The third, novel case involved feeding seawater into a falling film evaporator (FFE), where the seawater is thermally separated into water vapor and concentrated brine. Here dissolved Si is removed by the evaporation process ^[181]. Figure 54 illustrates simplified flowsheet of both seawater based system configurations.

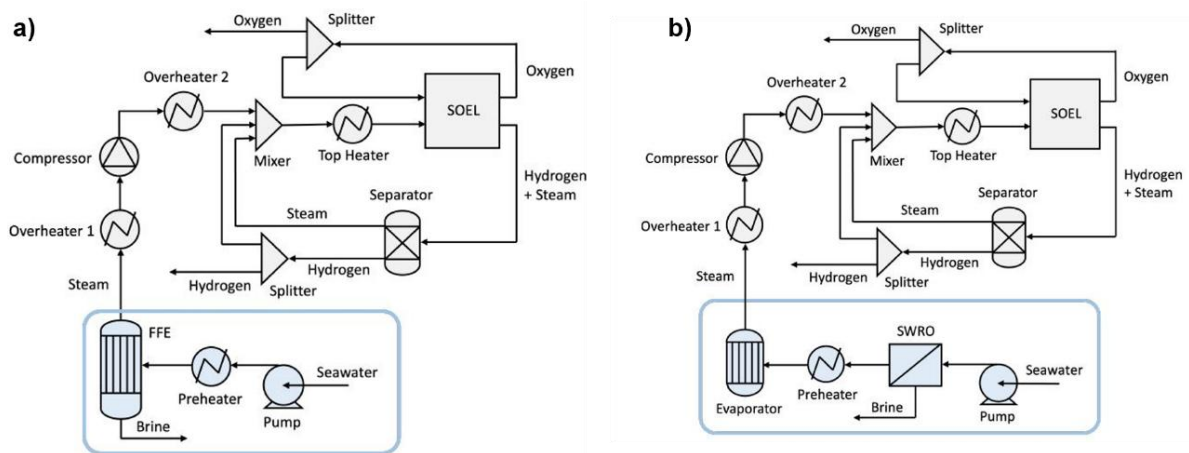


Figure 54 Simplified flowsheets of seawater utilization in SOEC systems for (a) the FFE and (b) the SWRO case.

6.4.2 Heat Demand and Integration

To optimize the thermal integration of the system, an optimized heat exchanger system was developed, enabling the utilization of the waste heat for its usage in preheating of the water evaporator. The temperatures and enthalpies of the hot and cold streams within the whole system are obtained. The composite curves of the hot and cold internal streams are presented in Figure 55. These curves represent the internal heat exchange potential within the system. The composite curves for the pure water conventional and the seawater SWRO based system are identical, as both share the same hot and cold stream configuration.

The flat section in the cold composite curve corresponds to the energy required for water evaporation, with a characteristic temperature hold observed around 100 °C. The following linear increase in temperature reflects the heat input required for recirculation and mixing of hydrogen and steam in the feedgas of the SOEC system.

In both the conventional and SWRO configurations, the heat duty required for evaporation is calculated as 206.8 kW. In contrast the seawater FFE system requires a higher heat duty for evaporation of 225.9 kW. On the one hand, the increased demand stems from the lower evaporation rate of 50 % in the FFE case, which results from the requirement to discharge the brine at 101.7 °C, which introduces additional cooling and associated energy. On the other hand, the elevated boiling point saline water requires more energy for the phase transition ^[182]. Together, this accounts for the approximately 8 % higher heating demand of the FFE case compared to the conventional and the SWRO based systems.

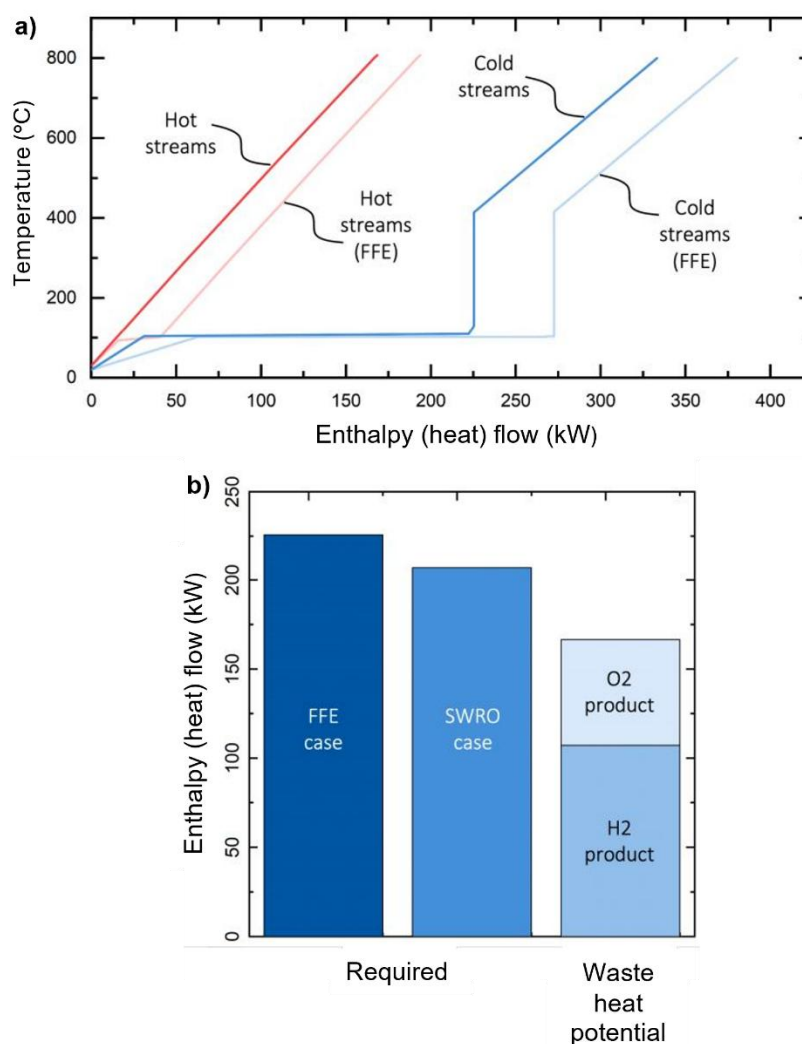


Figure 55 (a) Composite curves showing the enthalpy requirements for seawater evaporation in the two process cases. (b) Comparison of the required enthalpy with the waste heat potential of the outgoing hot streams. In the FFE case, the cold and hot composite streams differ from the conventional and SWRO based systems due to the direct evaporation of salt containing

seawater. However, in all cases, the available heat from the hot composite streams is insufficient to fully supply the system thermal requirements under the chosen operation conditions of $-1 \text{ A}\cdot\text{cm}^{-2}$ and an operation temperature of 800°C . Specifically, the thermal energy provided by either the oxygen or the hydrogen product stream from the SOEC is inadequate to evaporate the water feed completely. Even the non permissible simultaneous use of the oxygen and hydrogen hot streams in one heat exchanger remains insufficient, as illustrated in Figure 55.

By operating the SOEC system at a higher current density or at the thermoneutral voltage hot product streams for full thermal self sufficiency might be realized ^[19]. However, operation at higher currents results in increases in degradation rates, which limits their practical applicability. ^[30, 120]

As the hot streams are not sufficient for both cases in the investigated system, external heat must be supplied. The FFE configuration requires a higher amount of external energy for heating compared to the conventional pure water and SWRO based systems as discussed above. Potential sources for this external heat include steam, external heat from solar thermal power or hot exhaust gases from industry ^[183-184].

For both the SWRO and FFE configuration, an optimized heat exchanger network was designed and evaluated. The optimized network for the FFE case is shown in Figure A 11 in the appendix. It is concluded that a total of 13 heat exchangers are needed, with 10 being critical for the technical implementation. The remaining 3 heat exchangers are required for air cooling of unused heat from the output streams (hydrogen, oxygen, brine). Through this network, approximately 33 % of the total external heat demand can be covered by internal heat recovery. From the optimized heat exchanger network, a remaining external heat demand of about 267 kW and a cooling demand of 72 kW are calculated for the complete process. As expected, the evaporation process itself accounts for 84 % of the total external heat requirement.

The optimized heat exchanger network for the SWRO case is shown in Figure A 12 in the appendix. From the designed network, only nine heat exchangers are needed, with seven necessary for the technical design. The two additional units serve again for air cooling of unused heat from the product gas streams. Compared to the FFE case, the number of necessary heat exchangers is reduced by three due to the unnecessary cooling of brine and the more efficient integration of the output flows. The remaining external heat demand for the SWRO configuration is around 248 kW with a cooling demand of 19 kW. In comparison to the FFE case, around 19 kW in external heating and 53 kW in cooling can be saved.

In summary, across all configurations, internal heat recovery is insufficient to fully supply the evaporation energy, and external heat or electricity is necessary. From a technical point, the FFE case is more complex compared to the SWRO case as it contains more components that

are exposed to salt containing water, including the FFE unit and brine cooling heat exchangers. Thus, these components need to be corrosive resistant and are more prone to technical failure. Furthermore, the FFE case has a higher external heat demand of around + 20 kW in comparison to the SWRO, primarily due to the greater energy required for evaporating saline water.

6.4.3 Electricity Demand

Next, the electric power demand of the system is evaluated, focusing on the major inputs which are the demand for pumps, compressors and the SOEC and the cleaning of seawater in the case of a SWRO configuration. It is assumed that the required external energy for evaporation (see chapter 6.4.2) is provided by external heat sources (e.g., industrial waste heat or solar thermal) and not by electrical energy. The results shown here already consider the optimized heat integration performed in the previous chapter. For all configurations, a stationary 1 MW SOEC system was used under a current load of $-1 \text{ A}\cdot\text{cm}^{-2}$ and operated at 800°C . Thus, the demand of electric power of the SOEC is constant at 1000 kW, referring to 34 kg/h of H_2 and 271 kg/h of oxygen produced.

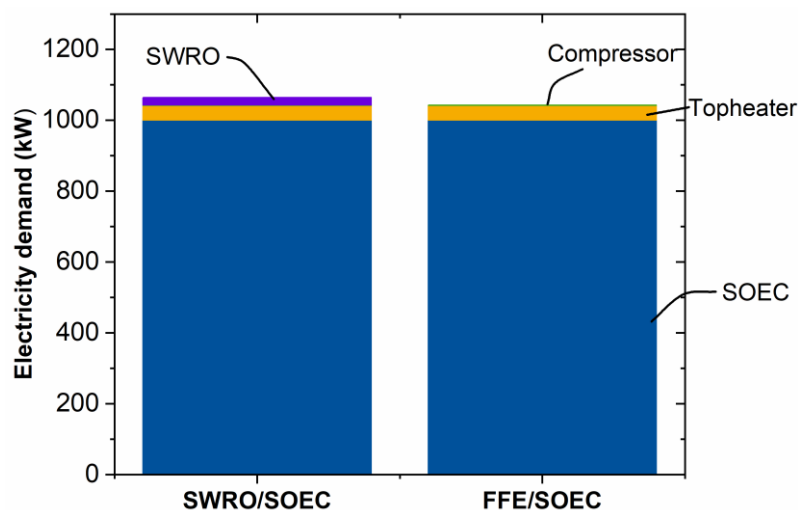


Figure 56 Electricity demand of the FFE/SOEC case and the SWRO/SOEC case for the direct utilization of seawater.

The total demand of electric power of the FFE case amounts to 1060.6 kW. Of this, 41.5 kW is required for the top heater and 19.1 kW for the system compressors and the rest to the SOEC itself. The demand for electric power from the pumps is found to be negligible. The SOEC accounts for most of the electricity demand with a relative contribution of 94 %. The other components account for the remaining 6 %. In the case of the SWRO configuration, the total electricity demand is 1082.6 kW. The pumps are still negligible. Like the FFE case, the SOEC accounts for most of the electricity demand with a relative amount of 92 %. The remaining 8 %

is attributed to auxiliary components and the SWRO unit. Figure 56 presents a graphical comparison of the electricity demand for both seawater configurations.

In conclusion, the SWRO based configuration requires approximately 22 kW more electrical power than the FFE case. As shown in section 6.4.2 the FFE case demands around 20 kW more in heat demand. Therefore, when considering the total external energy input (electric and thermal), both system configurations exhibit nearly an equivalent total energy demand.

6.4.4 Techno Economic Evaluation

For the economic evaluation, the two developed cases for seawater utilization in SOEC systems are compared with a conventional pure water utilizing SOEC system. The levelized cost of hydrogen (LCOH) values are calculated using ASPEN, based on the input parameters discussed in chapter 5.5. For the conventional SOEC system, the hydrogen production rates, and the heat integration strategies developed in the seawater cases are also applied, ensuring a valid comparison of water source effects on analysis.

Figure 57a presents the resulting LCOH values. All configurations exhibit values around 5 \$/kg H₂. The LCOH value for a conventional 1 MW SOEC system with freshwater utilization is 4.95 \$/kg H₂. This is consistent with literature studies on similar plant sizes and at similar electricity prices where values between 3.5 and 7 \$/kg H₂ are reported [71, 185-186]. Here the author wants to note that a scale up reduces the LCOH significantly. For instance, the scale up to 1 GW SOEC system could enable a significant reduction to around 2 \$/kg H₂ [68].

The LCOH for the SWRO based case yields 4.95 \$/kg H₂, which is identical to the one for the conventional SOEC system. This is expected as in the freshwater case the price of the freshwater is included whereas in the SWRO case, the purification of freshwater is added. Even though the SWRO unit increases the electrical demand as shown in the section before and higher service and maintenance costs are included, the costs for the water supply are zero in contrast to the costs for freshwater. The FFE configuration exhibits the lowest price of 4.90 \$/kg H₂. This is primarily due to the need for lower electricity demand compared to the SWRO configuration. Additionally, no money is accounting for freshwater compared to the conventional freshwater SOEC. However, this economic advantage is highly sensitive to the cost assumption for external heat which is assumed to be zero here because of integration into industry. Further in the thesis, a sensitive analysis is performed considering higher external heat costs (see Figure 58).

A breakdown of the cost structure for the FFE based seawater SOEC system is presented in Figure 57b, comparing the annualized capital expenditure (CAPEX) over a 20 year lifetime with the non discounted average annual operating expenditure (OPEX). The CAPEX costs only contribute to a minority of the total yearly costs and, consequently, to LCOH. The dominant cost component is the OPEX due to the high electricity costs. Consequently, the electricity

costs are the main driver of the LCOH which explains the similar LCOH values for all three cases. Stack replacement costs are the second largest contribution due to the relatively high degradation rates reported for state-of-the-art Ni containing fuel electrode based SOECs as discussed in Chapter 2.3.

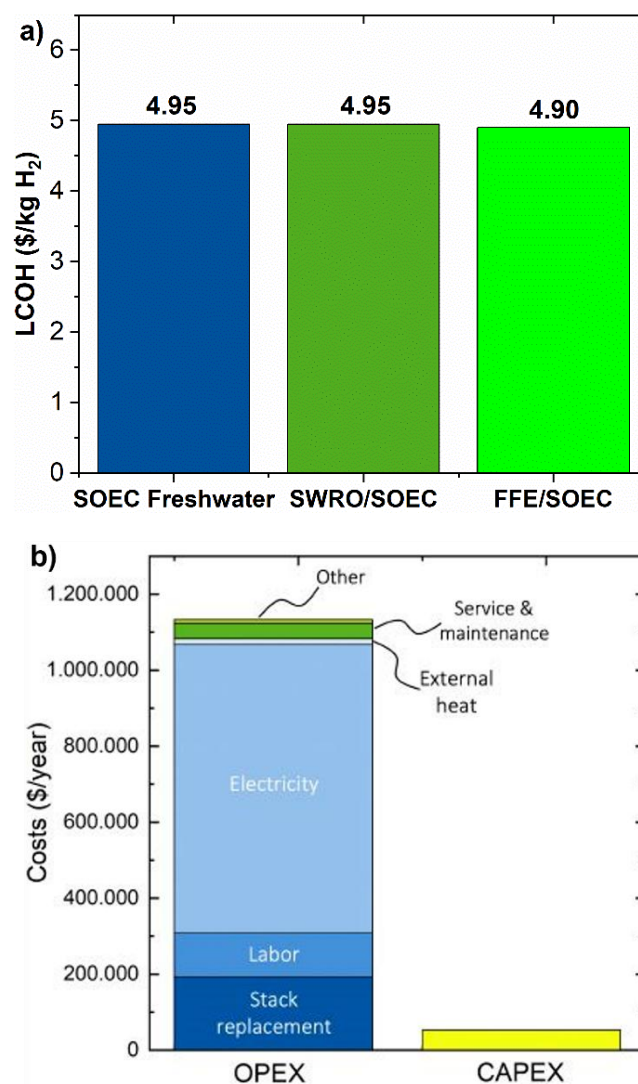


Figure 57 (a) LCOH values in SOEC system operated with fresh water and the two cases for seawater utilization. (b) Breakdown of the annualized OPEX and CAPEX for the FFE/SOEC case per year.

To further assess system sensitivity, a parametric analysis of key economic factors was performed. Firstly, the electricity price variation is evaluated as shown in Figure 58a. As expected, all three configurations are highly sensitive to a change in electricity prices, and a significant effect to the LCOH is visible. Thus, the electricity demand of the SOEC component is the primary cost driver and limits the potential for improvement. This underlines the dependence of the economic viability of electrolysis on the electricity prices ^[187-189]. Notably, at

higher electricity prices, the FFE based seawater configuration becomes economically more favorable compared to the SWRO case, due to its lower overall electricity demand. With a decrease in electricity prices, the SWRO case becomes more since the electricity demand of the SWRO unit becomes less economically impactful. Thus, in regions where the electricity price is high, the FFE case will gain economic viability compared to the SWRO case and in regions with low energy prices, the SWRO case closes the gap to the FFE case.

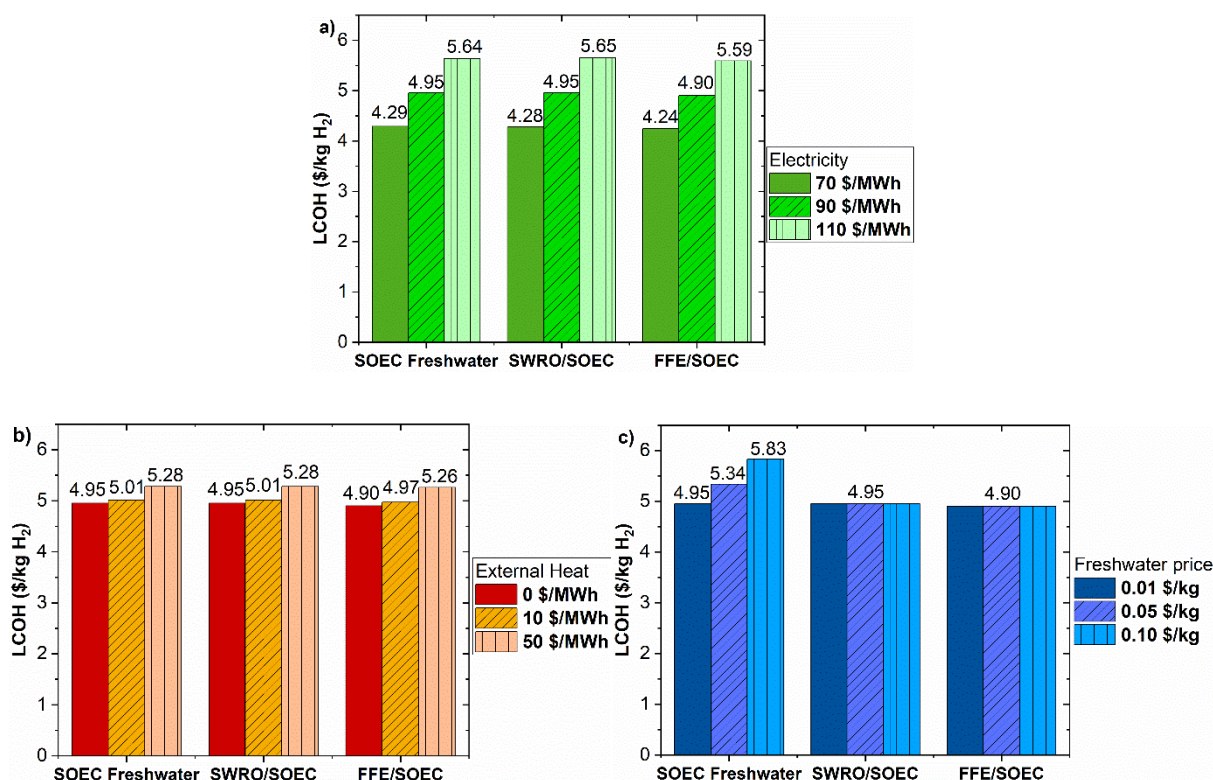


Figure 58 Sensitivity analysis of (a) the electricity price, (b) the external heating costs and (c) the freshwater price for both investigated seawater cases and the freshwater operating system.

Secondly, the price of waste heat is discussed, as shown in Figure 58b. With an increase in external heat prices, the LCOH is moderately increasing for the conventional pure water, the SWRO and the FFE configurations. In comparison to the electricity price, the influence of the external heat price is significantly lower. Furthermore, with an increase in external heat prices, the LCOH of the FFE case approaches that of the SWRO case, reducing its economic advantage. In regions where low costs of external heat are present, such as industrial waste heat, the FFE case is particularly favorable compared to the SWRO based SOEC system.

For the conventional case, a sensitive analysis of the price of freshwater is shown in Figure 58c. Here, freshwater prices significantly influence the LCOH. Thus, economically speaking, the use of seawater in the FFE and SWRO case becomes more feasible with an increase in freshwater prices. This highlights the potential economic benefit of seawater based

approaches (FFE and SWRO), especially in regions with limited freshwater availability or high freshwater prices.

In summary, direct utilization of seawater is economically competitive against the conventional freshwater electrolysis and gets more economically advantageous with increasing freshwater prices. This is due to the high contribution of the electricity price to the LCOH in all cases. Furthermore, in regions where the electricity price is low and the price of external heat is high, the SWRO case is economically like the FFE case. In regions where the electricity price is high and the external heat price is low, the FFE case gains an economic advantage over the SWRO configuration. Thus, the economic risk of using seawater in SOEC is considered low and different evaporator systems can be used in different regions. Again here the author wants to note that this is under the assumption that silicon impurities are filtered out by both seawater based configurations which was the main degradation issue in seawater operation discussed in chapter 6.2 ^[180-181]. However, the conventional SOEC and the SWRO system are already well known and thus the technical risk is considered low for the SWRO case. In contrast, the FFE case is not yet well established and is technically more demanding due to the need for more heat exchangers and corrosive resistant components. Furthermore, no practical data about the coupling of a FEE with a SOEC is available, for instance in terms of maintenance and difficulties in technical development.

7 Summary and Outlook

The primary objective of this thesis was to investigate the feasibility of direct salt containing waters usage for hydrogen production in solid oxide electrolysis cells (SOECs). Specifically, the operation with real seawater and saturated sodium chloride solution were compared to pure water operation in terms of performance and stability on the laboratory scale. The initial performance was compared by measuring current density voltage (iV) curves at different operation conditions and activation energy analysis. Stability studies were conducted for up to 1000 hours at a current density of $-1 \text{ A}\cdot\text{cm}^{-2}$. During the stability measurements, every 100 hours iV curves and electrochemical impedance spectroscopy (EIS) measurements were recorded. The EIS data were fitted to an equivalent circuit model (ECM) developed in this work. The ECM includes an inductance in series with a resistor and four individual RQ elements representing the electrochemical processes occurring in the Ni-YSZ fuel electrode supported SOECs.

Two different cell production batches were used throughout the study. To establish a robust baseline, several pure water measurements were performed first. Differences in the degradation behavior between two cell batches were analyzed. The older batch exhibited silicon (Si) poisoning which was associated with a rapid increase in cell voltage during the first 200 hours of operation, leading to higher degradation rates compared to the newer cell batch. The Si poisoning corresponded to an increase in the high frequency processes RQ_1 and RQ_2 related to the electrochemical reaction at the Ni-YSZ fuel electrode including the charge transfer and the ion transport. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) analysis of a cell operated for 1000 hours confirmed the presence of Si incorporated into Ni particles in the older cell batch. Furthermore, higher Ni agglomeration and depletion were observed post operation in the Si contaminated cells. Based on these findings, only cells from the same production batch were compared in terms of their stability using different water sources.

For the investigation of direct seawater utilization in SOECs, natural seawater gathered from the coast of the island Texel in the Netherlands was used. In comparison to pure water operation, similar initial performances and activation energies of the area specific resistance (ASR) were found, indicating no influence by seawater utilization. However, during long term operation, seawater operation exhibited a higher degradation rate compared to pure water operation. This is due to an accelerated voltage increase between 400 and 600 hours of operation corresponding to an increase in the resistance of the high frequency processes RQ_1 and RQ_2 . Post test analysis confirmed the transport of salt impurities to the Ni-YSZ fuel electrode surface and the electrochemically active layer of the Ni-YSZ fuel electrode adjacent to the electrolyte. Si poisoning was found in the Ni-YSZ fuel electrode, which is believed to be

the main cause of the accelerated degradation exhibited for seawater operation. Furthermore, no significant Zr phase densification is observed in the Ni-YSZ fuel electrode after 1000 hours of operation, which is contradictory to pure water operation. This observation suggests that the transport of certain impurities might prevent Zr agglomeration, especially as it has been reported that CaO is increasing the hydrothermal stability of YSZ and could decrease Ni mobility ^[167]. Nonetheless, further studies are required to confirm the mechanisms underlying this potential effect.

To investigate the effects of wastewater with higher sodium chloride content, such as that found in polycarbonate production, and to gather information into accelerated stress test for seawater utilization, a concentrated sodium chloride solution was employed in the SOECs. Like the findings for seawater, no negative impact on the initial performance and activation energies was observed compared to pure water operation. In contrast, a higher degradation rate was recorded in a stability test over 1000 hours for a NaCl operated cell. This is due to a more pronounced increase in voltage after 400 hours of operation compared to a pure water cell. From EIS analysis, the increase is mainly due to the high frequency process RQ_1 and RQ_2 , which are associated with the electrochemical reaction at the Ni-YSZ fuel electrode. Post test analysis revealed salt deposits on the Ni-YSZ fuel electrode surface and the active electrode cross section. Notably, sodium was detected in the form of sodium carbonate species rather than sodium chloride. Thus, a mechanism was proposed, which included the formation of HCl and NaOH caused by the transport of NaCl to the Ni-YSZ fuel electrode. The accelerated degradation is connected to the poisoning of the electrode by the formed HCl, as described in the literature ^[32, 34, 93, 176]. Poisoning by HCl can lead to higher agglomeration of the Ni phase which was seen by SEM-EDX post characterization of the Ni-YSZ fuel electrode cross section ^[93, 176-178].

From the laboratory experiments conducted, it is evident that salt transport to the cell and silicon poisoning are critical degradation factors when utilizing seawater or industrial wastewater in SOEC systems. At the system level, particular attention must be given to the evaporation section, as conventional evaporators are prone to salt cloaking and could be damaged by direct saltwater usage. Thus, a novel system design, including a falling film evaporator (FFE) coupled to a SOEC system and the required balance of plant (BOP) for direct seawater utilization, was developed. The FFE configuration was technically and economically evaluated and benchmarked against a seawater reverse osmosis (SWRO) unit coupled with a SOEC and a conventional freshwater SOEC system. The results indicate that both seawater based configurations (FFE/SOEC and SWRO/SOEC) are economically competitive against a pure water operated SOEC system and become advantageous as freshwater prices rise. Comparing the FFE/SOEC case to the SWRO/SOEC case shows that the FFE system requires more heating energy due to the higher evaporation enthalpy of the seawater, while the

SWRO/SOEC configuration requires more electrical energy to operate the additional SWRO unit. Consequently, the novel designed FFE/SOEC is economically advantageous in regions with access to low cost heat sources. However, the novel FFE/SOEC system carries increased technical risk, as it introduces more complexity due to an increase in heat exchanger numbers and components that need to be corrosive resistant. In contrast, the SWRO/SOEC system offers a more mature industrial proven approach. The choice between the two systems depends on the local cost of electricity and heat, as well as risk assessments.

In summary, the operation of an SOEC with steam produced from salt containing waters should be regarded as critical due to the salt and impurity transport to the SOEC and the associated technical difficulties, which contrasts prior literature publications [9, 14-15, 94]. Silicon containing water, such as seawater, can accelerate the degradation in SOECs due to poisoning of the Ni-YSZ fuel electrode. The transport of sodium chloride to the cell accelerates the degradation of Ni-YSZ fuel electrodes. A degradation mechanism, including the formation of HCl, is proposed in this thesis. Thus, these impurities should be avoided and removed before reaching the electrochemical active parts of a SOEC. Interestingly, seawater utilization also shows a beneficial effect, as it prevented Zr densification in the Ni-YSZ fuel electrode compared to pure water operation. From a technical and economic perspective, the utilization of seawater in SOECs is feasible. Moreover, direct evaporation and thermal purification using a falling film evaporator can be economically when low cost waste heat is available, even though the technical complexity is higher compared to a SWRO coupled with a conventional evaporator. Further studies should focus on the development of materials that remain stable against critical impurities during seawater or wastewater operation. Ni free fuel electrodes are especially promising in preventing degradation issues of Ni poisoning or accelerated agglomeration. Another promising approach is the application of proton conducting electrolysis cells where steam is used on the oxygen side, which typically does not contain Ni [190-191]. Additionally, the beneficial effect of seawater on Zr phase densification in Ni-YSZ fuel electrodes should be investigated in greater detail, and the responsible substances should be assessed. Based on the results in this thesis, especially the impact of transported CaO should be evaluated. At the system level the potential of combining purification and evaporation into a single process step should be explored and novel concepts should be developed. Suitable economic locations for SOEC systems coupled with evaporator/purification systems for seawater or wastewater utilization should be identified. For a potential scale up of the FFE/SOEC system and a clear assessment of issues, collaboration with the manufacturing industry will be necessary.

8 Literature

- [1] M. B. Mogensen, F. Mondt and G. Mogensen in *High-temperature electrolysis—general overview*, IOP Publishing, 2023, pp. 1-1-1-20.
- [2] S. Song, H. Lin, P. Sherman, X. Yang, C. P. Nielsen, X. Chen and M. B. McElroy, *Nature Communications* **2021**, *12*, 6953.
- [3] P. Burek, Y. Satoh, G. Fischer, M. T. Kahil, A. Scherzer, S. Tramberend, L. F. Nava, Y. Wada, S. Eisner and M. Flörke, **2016**.
- [4] S. a. C. O. United Nations Educational, *The United Nations World Water Development Report 2023: partnerships and cooperation for water*, Place de Fontenoy, 75352 Paris 07 SP, France, **2023**.
- [5] C. He, Z. Liu, J. Wu, X. Pan, Z. Fang, J. Li and B. A. Bryan, *Nature Communications* **2021**, *12*, 4667.
- [6] W. Bank, *High and dry: Climate change, water, and the economy*, The World Bank, **2016**.
- [7] Solargis and W. B. Group, *Global Solar Atlas 2.0*, **2025**, <https://globalsolaratlas.info>, accessed 07.09.2025.
- [8] J. Guo, Y. Zheng, Z. Hu, C. Zheng, J. Mao, K. Du, M. Jaroniec, S.-Z. Qiao and T. Ling, *Nature Energy* **2023**, *8*, 264-272.
- [9] C. K. Lim, Q. Liu, J. Zhou, Q. Sun and S. H. Chan, *Journal of Power Sources* **2017**, *342*, 79-87.
- [10] H. Xie, Z. Zhao, T. Liu, Y. Wu, C. Lan, W. Jiang, L. Zhu, Y. Wang, D. Yang and Z. Shao, *Nature* **2022**, *612*, 673-678.
- [11] L. Yu, Q. Zhu, S. Song, B. McElhenny, D. Wang, C. Wu, Z. Qin, J. Bao, Y. Yu, S. Chen and Z. Ren, *Nature Communications* **2019**, *10*, 5106.
- [12] H. Shi, T. Wang, J. Liu, W. Chen, S. Li, J. Liang, S. Liu, X. Liu, Z. Cai, C. Wang, D. Su, Y. Huang, L. Elbaz and Q. Li, *Nature Communications* **2023**, *14*, 3934.
- [13] J. Corbin, M. Jones, C. Lyu, A. Loh, Z. Zhang, Y. Zhu and X. Li, *RSC Advances* **2024**, *14*, 6416-6442.
- [14] Z. Liu, B. Han, Z. Lu, W. Guan, Y. Li, C. Song, L. Chen and S. C. Singhal, *Applied Energy* **2021**, *300*, 117439.
- [15] H. Pan, A. Wu, S. F. Au, Y. Yang, Z. Song, Z. Liu, X. Gong and W. Guan, *Sustainable Energy & Fuels* **2023**, *7*, 3333-3341.
- [16] R. Peters, N. Kruse, W. Tiedemann, I. Hoven, R. Deja, D. Schäfer, F. Kunz and R.-A. Eichel, *ECS Transactions* **2023**, *111*, 1657.
- [17] L. Dittrich, Tailoring of the synthesis gas composition during high-temperature co-electrolysis, *RWTH Aachen University* **2021**.

- [18] M. Yu, E. Budiyanto and H. Tüysüz, *Angewandte Chemie International Edition* **2022**, *61*, e202103824.
- [19] A. Hauch, R. Küngas, P. Blennow, A. B. Hansen, J. B. Hansen, B. V. Mathiesen and M. B. Mogensen, *Science* **2020**, *370*, eaba6118.
- [20] H. Böhm, S. Moser, S. Puschnigg and A. Zauner, *International Journal of Hydrogen Energy* **2021**, *46*, 31938-31951.
- [21] S. E. Wolf, F. E. Winterhalder, V. Vibhu, L. G. J. de Haart, O. Guillon, R.-A. Eichel and N. H. Menzler, *Journal of Materials Chemistry A* **2023**, *11*, 17977-18028.
- [22] C. Graves, S. D. Ebbesen, M. Mogensen and K. S. Lackner, *Renewable and Sustainable Energy Reviews* **2011**, *15*, 1-23.
- [23] Q. Fang, C. E. Frey, N. H. Menzler and L. Blum, *Journal of The Electrochemical Society* **2018**, *165*, F38.
- [24] A. Léon, A. Micero, B. Ludwig and A. Brisse, *Journal of Power Sources* **2021**, *510*, 230346.
- [25] G. Rinaldi, S. Diethelm, E. Oveisi, P. Burdet, J. Van herle, D. Montinaro, Q. Fu and A. Brisse, *Fuel Cells* **2017**, *17*, 541-549.
- [26] J. Schefold, A. Brisse, M. Zahid, J. P. Ouweltjes and J. U. Nielsen, *ECS Transactions* **2011**, *35*, 2915.
- [27] K. Chen and S. P. Jiang, *Journal of The Electrochemical Society* **2016**, *163*, F3070.
- [28] P. Moçoteguy and A. Brisse, *International Journal of Hydrogen Energy* **2013**, *38*, 15887-15902.
- [29] M. B. Mogensen, M. Chen, H. L. Frandsen, C. Graves, A. Hauch, P. V. Hendriksen, T. Jacobsen, S. H. Jensen, T. L. Skaftø and X. Sun, *Fuel Cells* **2021**, *21*, 415-429.
- [30] R. Knibbe, M. L. Traulsen, A. Hauch, S. D. Ebbesen and M. Mogensen, *Journal of The Electrochemical Society* **2010**, *157*, B1209.
- [31] S. E. Wolf, V. Vibhu, E. Tröster, I. C. Vinke, R.-A. Eichel and L. G. J. de Haart, *Solid Oxide Electrolysis Cells* **2022**, *15*, 5449.
- [32] G. Jeanmonod, S. Diethelm and J. Van herle, *Journal of Power Sources* **2021**, *506*, 230247.
- [33] Y. Tao, J. Shao and S. Cheng, *ACS Applied Materials & Interfaces* **2016**, *8*, 17023-17027.
- [34] F. N. Cayan, M. Zhi, S. R. Pakalapati, I. Celik, N. Wu and R. Gemmen, *Journal of Power Sources* **2008**, *185*, 595-602.
- [35] M. A. Laguna-Bercero, R. Campana, A. Larrea, J. A. Kilner and V. M. Orera, *Journal of Power Sources* **2011**, *196*, 8942-8947.
- [36] A. Momma, T. Kato, Y. Kaga and S. Nagata, *Journal of the Ceramic Society of Japan* **1997**, *105*, 369-373.
- [37] V. Brichzin, J. Fleig, H. U. Habermeier, G. Cristiani and J. Maier, *Solid State Ionics* **2002**, *152-153*, 499-507.

- [38] N. C. Kani, S. Olusegun, R. Chauhan, J. A. Gauthier and M. R. Singh, *EES Catalysis* **2024**, 2, 507-521.
- [39] R. O'Hayre, S.-W. Cha, W. Colella and F. B. Prinz in *Chapter 3: Fuel Cell Reaction Kinetics*, **2016**, pp. 77-116.
- [40] R. O'Hayre, S.-W. Cha, W. Colella and F. B. Prinz in *Chapter 4: Fuel Cell Charge Transport*, **2016**, pp. 117-166.
- [41] R. O'Hayre, S.-W. Cha, W. Colella and F. B. Prinz in *Chapter 5: Fuel Cell Mass Transport*, **2016**, pp. 167-202.
- [42] K. Yamahara, C. P. Jacobson, S. J. Visco and L. C. De Jonghe, *ECS Proceedings Volumes* **2003**, 2003, 187.
- [43] E. Ivers-Tiffée, A. Weber and D. Herbstritt, *Journal of the European Ceramic Society* **2001**, 21, 1805-1811.
- [44] L. Abadlia, F. Gasser, K. Khalouk, M. Mayoufi and J. G. Gasser, *Review of Scientific Instruments* **2014**, 85.
- [45] A. J. Bard, L. R. Faulkner and H. S. White, *Electrochemical methods: fundamentals and applications*, John Wiley & Sons, **2022**.
- [46] J. Böckris, A. Reddy and M. Gamboa-Aldeco, *Modern Electrochemistry, 2A: Fundamentals of Electrodics* **2000**.
- [47] T. Jacobsen, P. V. Hendriksen and S. Koch, *Electrochimica Acta* **2008**, 53, 7500-7508.
- [48] S. Primdahl and M. Mogensen, *Journal of the electrochemical Society* **1998**, 145, 2431.
- [49] Y. Barsukov and J. R. Macdonald, *Characterization of materials* **2012**, 2, 898-913.
- [50] M. E. Orazem and B. Tribollet in *Complex Variables*, **2017**, pp. 1-23.
- [51] C. F. Mänken, J. Uecker, D. Schäfer, L. G. J. De Haart and R.-A. Eichel, *Journal of The Electrochemical Society* **2024**, 171, 064503.
- [52] T. Frömling, Y. Liu, A.-P. Hoang, M. Gehringer, S. Steiner, M. Zhuk, J. Glaum and B.-X. Xu, *Journal of Materiomics* **2022**, 8, 556-569.
- [53] K. Fitzek, U. de Haart, Q. Fang and W. Lehnert, *Journal of The Electrochemical Society* **2022**, 169, 014501.
- [54] W. Mulder, J. Sluyters, T. Pajkossy and L. Nyikos, *Journal of electroanalytical chemistry and interfacial electrochemistry* **1990**, 285, 103-115.
- [55] C. Plank, T. Rüther, L. Jahn, M. Schamel, J. P. Schmidt, F. Ciucci and M. A. Danzer, *Journal of Power Sources* **2024**, 594, 233845.
- [56] E. Ivers-Tiffée and A. Weber, *Journal of the Ceramic Society of Japan* **2017**, 125, 193-201.
- [57] A. Allagui and A. Elwakil, *Advanced Theory and Simulations*, **2025**, 8, e00792.
- [58] M. Nohl, G. Raut, S. E. Wolf, T. Duyster, L. Dittrich, I. C. Vinke, R.-A. Eichel and L. G. J. De Haart, *ECS Transactions* **2021**, 103, 1403.

- [59] A. Leonide, V. Sonn, A. Weber and E. Ivers-Tiffée, *Journal of The Electrochemical Society* **2008**, *155*, B36.
- [60] A. Ploner, A. Hagen and A. Hauch, *Fuel Cells* **2017**, *17*, 498-507.
- [61] V. Sonn, A. Leonide and E. Ivers-Tiffée, *Journal of The Electrochemical Society* **2008**, *155*, B675.
- [62] P. Caliendo, A. Nakajo, S. Diethelm and J. Van herle, *Journal of Power Sources* **2019**, *436*, 226838.
- [63] Z. Wuillemin, Y. Antonetti, C. Beetschen, O. Millioud, S. Ceschini, H. Madi and J. Van herle, *ECS Transactions* **2013**, *57*, 561.
- [64] CEA-Liten, *MultiPLHY*, **2025**, <https://multiplhy-project.eu/Pages/About.aspx>, accessed 10.09.2025.
- [65] P. C. K. Vesborg and T. F. Jaramillo, *RSC Advances* **2012**, *2*, 7933-7947.
- [66] J. Uecker, I. D. Unachukwu, V. Vibhu, I. C. Vinke, R.-A. Eichel and L. B. de Haart, *Electrochimica Acta* **2023**, *452*, 142320.
- [67] J. Uecker, I. D. Unachukwu, V. Vibhu, I. C. Vinke, L. G. J. de Haart and R.-A. Eichel, *ChemElectroChem* **2024**, *11*, e202300617.
- [68] J. H. Prosser, B. D. James, B. M. Murphy, D. S. Wendt, M. J. Casteel, T. L. Westover and L. T. Knighton, *International Journal of Hydrogen Energy* **2024**, *49*, 207-227.
- [69] H. Böhm, A. Zauner, S. Goers, R. Tichler and P. Kroon, *European Commission Research & Innovation* **2018**, *10*, 12-25.
- [70] X. Wang, L. Shao, S. Hu, Z. Li, H. Guo, J. Zhang, Y. Zhao, X. Lin, B. Nie, Z. Hu and J. Zou, *Energy & Environmental Science* **2024**, *17*, 8429-8456.
- [71] M. Naeini, J. S. Cotton and T. A. Adams, *Frontiers in Energy Research* **2022**, *10*, 1015465.
- [72] J. Yates, R. Daiyan, R. Patterson, R. Egan, R. Amal, A. Ho-Baille and N. L. Chang, *Cell Reports Physical Science* **2020**, *1*.
- [73] S. Lechtenböhmer, S. Samadi, A. Leipprand and C. Schneider, **2019**.
- [74] R. Geres, A. Kohn, S. Lenz, F. Ausfelder, A. M. Bazzanella and A. Möller in *Roadmap Chemie 2050. Auf dem Weg zu einer treibhausgasneutralen chemischen Industrie in Deutschland.*, **2023**, FutureCamp Climate GmbH and DECHEMA.
- [75] M. A. Khan, T. Al-Attas, S. Roy, M. M. Rahman, N. Ghaffour, V. Thangadurai, S. Larter, J. Hu, P. M. Ajayan and M. G. Kibria, *Energy & Environmental Science* **2021**, *14*, 4831-4839.
- [76] F.-Y. Gao, P.-C. Yu and M.-R. Gao, *Current Opinion in Chemical Engineering* **2022**, *36*, 100827.
- [77] S. Dresch, F. Dionigi, M. Klingenhof and P. Strasser, *ACS Energy Letters* **2019**, *4*, 933-942.
- [78] W. Tong, M. Forster, F. Dionigi, S. Dresch, R. Sadeghi Erami, P. Strasser, A. J. Cowan and P. Farràs, *Nature Energy* **2020**, *5*, 367-377.

- [79] J. N. Hausmann, R. Schlögl, P. W. Menezes and M. Driess, *Energy & Environmental Science* **2021**, 14, 3679-3685.
- [80] Y. Kuang, M. J. Kenney, Y. Meng, W. H. Hung, Y. Liu, J. E. Huang, R. Prasanna, P. Li, Y. Li, L. Wang, M. C. Lin, M. D. McGehee, X. Sun and H. Dai, *Proc Natl Acad Sci U S A* **2019**, 116, 6624-6629.
- [81] P. Farràs, P. Strasser and A. J. Cowan, *Joule* **2021**, 5, 1921-1923.
- [82] K. M. Conroy, F. Chen, O. H. Tuovinen and K. M. Mancl, *Applied engineering in agriculture* **2020**, 36, 33-37.
- [83] A. Krzyżanowska, E. Milchert and M. Bartkowiak, *Polish Journal of Chemical Technology* **2014**, 16, 86-90.
- [84] X. Liu, Z. Zhang, L. Zhang, S. Bu, W. Xu, C. Shi, J. Fang and C. Xu, *Chemical Engineering Research and Design* **2021**, 176, 194-201.
- [85] P. D. Ooms, A. Bulan, R. D. Weber, J. D. Rechner and M. D. Traving in *Verfahren zur Herstellung von Polycarbonat*, **2015**.
- [86] K. Meier, *International Journal of Energy and Environmental Engineering* **2014**, 5, 104.
- [87] A. Hauch, S. D. Ebbesen, S. H. Jensen and M. Mogensen, *Journal of The Electrochemical Society* **2008**, 155, B1184.
- [88] S. D. Ebbesen, C. Graves, A. Hauch, S. H. Jensen and M. Mogensen, *Journal of The Electrochemical Society* **2010**, 157, B1419.
- [89] A. Hauch, S. H. Jensen, J. B. Bilde-Sørensen and M. Mogensen, *Journal of The Electrochemical Society* **2007**, 154, A619.
- [90] S. D. Ebbesen, R. Knibbe and M. Mogensen, *Journal of The Electrochemical Society* **2012**, 159, F482.
- [91] S. D. Ebbesen and M. Mogensen, *Journal of Power Sources* **2009**, 193, 349-358.
- [92] J. Bao, G. N. Krishnan, P. Jayaweera, J. Perez-Mariano and A. Sanjurjo, *Journal of Power Sources* **2009**, 193, 607-616.
- [93] J. P. Trembly, R. S. Gemmen and D. J. Bayless, *Journal of Power Sources* **2007**, 169, 347-354.
- [94] X. Luo, A. Wu, J. Sang, N. Huang, B. Han, C. Wang, Y. Gao, W. Guan and S. C. Singhal, *International Journal of Hydrogen Energy* **2023**, 48, 10359-10367.
- [95] A. Jakhrani, S. Samo, H. R. Sobuz, M. A. Uddin, M. Ahsan and N. M. S. Hasan, *International Journal of Structural and Civil Engineering* **2012**, 1, 61-69.
- [96] M. Hahn, S. Schindler, L.-C. Triebs and M. A. Danzer, *Batteries* **2019**, 5, 43.
- [97] S. van der Walt, J. L. Schönberger, J. Nunez-Iglesias, F. Boulogne, J. D. Warner, N. Yager, E. Gouillart and T. Yu, *PeerJ* **2014**, 2, e453.
- [98] Y. Zhao, H. Xue, X. Jin, B. Xiong, R. Liu, Y. Peng, L. Jiang and G. Tian, *International Journal of Hydrogen Energy* **2021**, 46, 38163-38174.

- [99] A. A. AlZahrani and I. Dincer, *Applied Energy* **2018**, 225, 471-485.
- [100] J. van Baten and AmsterCHEM, *Python Unit Operation*, **2025**, <https://www.amsterchem.com/pythonunitoperation.html>, accessed 01.05.2025.
- [101] S. Chuaprasert, P. L. Douglas and M. H. Nguyen, *Journal of Food Engineering* **1999**, 39, 261-267.
- [102] M. M. Awad and E.-S. R. Negeed, *Proceedings of the International Water Technology Conference, IWTC12*, **2008**.
- [103] G. Micale, A. Cipollina and L. Rizzuti, *Seawater Desalination: Conventional and Renewable Energy Processes* **2009**, 1-15.
- [104] Z. Yu, S. Li, Y. Chen, X. Zhang, J. Chu, Y. Zhang and S. C. Tan, *Desalination* **2022**, 539, 115942.
- [105] M. S. Heike Glade, Detlef Taprogge in *Atlas zur Wasserentsalzung: Eine Zusammenfassung von 22 Technologien nach neuartigem Klassifizierungsansatz*, **2022**.
- [106] Veolia Water Solutions & Technologies, Sirion™, **2025** <https://www.veoliawatertech.com/en/solutions/technologies/sirion>, accessed 22.04.2025.
- [107] T. Kaghazchi, M. Mehri, M. T. Ravanchi and A. Kargari, *Desalination* **2010**, 252, 135-142.
- [108] P. Stephan, S. Kabelac, M. Kind, D. Mewes, K. Schaber and T. Wetzel, *VDI-Wärmeatlas: Fachlicher Träger VDI-Gesellschaft Verfahrenstechnik und Chemieingenieurwesen*, Springer-Verlag, **2019**.
- [109] D. Jang, J. Kim, D. Kim, W.-B. Han and S. Kang, *Energy Conversion and Management* **2022**, 258, 115499.
- [110] A. Aydemir, T. Fleiter, D. Schilling and M. Fallahnejad, *ECEEE Industrial Summer Study Proceedings; European Council for an Energy-Efficient Economy—ECEEE: online* **2020**, 30.
- [111] C. Li, *Degradation Behavior of Ni-YSZ Fuel Electrodes in SOEC*, Research Report, FZ Jülich/RWTH Aachen **2022**.
- [112] N. Eyckeler, *Multiphysics modeling of degradational behavior in high-temperature electrolysis cells based on experimental studies*, Master Thesis, FZ Jülich/RWTH Aachen **2024**.
- [113] N. Eyckeler, *Influence of the use of steam generated from seawater on the degradation of commercial Ni-YSZ solid oxide electrolysis cells*, Research Report, FZ Jülich/RWTH Aachen **2023**.
- [114] J. Uecker, L. Nohl, V. Vibhu, J.-P. Poc, P. Chakraborty, I. C. Vinke, S. Basak, L. G. J. de Haart and R.-A. Eichel, *Journal of Power Sources* **2025**, 633, 236390.
- [115] A. Hauch, S. Pylypko, G. Cubizolles and J. Mouginn, *ECS Transactions* **2021**, 103, 437.
- [116] A. Akter, J. R. Mulligan, H. Grande, U. Pal, S. N. Basu and S. Gopalan, *Journal of Power Sources* **2023**, 572, 233093.

- [117] Y. Tian, P. Wu, X. Zhang, L. Ding, Y. Li and X. Wu, *Ionics* **2022**, 28, 801-812.
- [118] S. E. Wolf, L. Dittrich, M. Nohl, T. Duyster, I. C. Vinke, R.-A. Eichel and L. G. J. de Haart, *Journal of The Electrochemical Society* **2022**, 169, 034531.
- [119] A. Hauch, K. Brodersen, M. Chen and M. B. Mogensen, *Solid State Ionics* **2016**, 293, 27-36.
- [120] M. P. Hoerlein, M. Riegraf, R. Costa, G. Schiller and K. A. Friedrich, *Electrochimica Acta* **2018**, 276, 162-175.
- [121] Q. Fang, L. Blum and D. Stolten, *Journal of The Electrochemical Society* **2019**, 166, F1320.
- [122] S. E. Wolf, V. Vibhu, E. Tröster, I. C. Vinke, R.-A. Eichel and L. G. J. de Haart, *Energies* **2022**, 15, 5449.
- [123] Q. Shao, D. Jin, Y. Lu, Y. Yu, L. Luo, X. Sun, C. Guan and J.-Q. Wang, *International Journal of Hydrogen Energy* **2024**, 57, 709-716.
- [124] X. Sun, P. V. Hendriksen, M. B. Mogensen and M. Chen, *Fuel Cells* **2019**, 19, 740-747.
- [125] C. Graves, S. D. Ebbesen, S. H. Jensen, S. B. Simonsen and M. B. Mogensen, *Nature Materials* **2015**, 14, 239-244.
- [126] M. Chen, Y.-L. Liu, J. J. Bentzen, W. Zhang, X. Sun, A. Hauch, Y. Tao, J. R. Bowen and P. V. Hendriksen, *Journal of The Electrochemical Society* **2013**, 160, F883.
- [127] J. Aicart in *Modeling and experimental validation of high temperature steam and carbon dioxide co-electrolysis-Modélisation et validation expérimentale d'un co-électrolyseur de la vapeur d'eau et du dioxyde de carbone à haute température*, Université de Grenoble, **2014**.
- [128] A. Hauch, *Solid oxide electrolysis cells: performance and durability*, Risø National Laboratory, **2008**.
- [129] A. Hauch, S. H. Jensen, S. Ramousse and M. Mogensen, *Journal of The Electrochemical Society* **2006**, 153, A1741.
- [130] L. André in *SOFC Modelling and Parameter Identification by Means of Impedance Spectroscopy*, Universität Karlsruhe Karlsruhe, Germany, **2010**.
- [131] M. Trini, A. Hauch, S. De Angelis, X. Tong, P. V. Hendriksen and M. Chen, *Journal of Power Sources* **2020**, 450, 227599.
- [132] A. Hauch, M. Mogensen and A. Hagen, *Solid State Ionics* **2011**, 192, 547-551.
- [133] T. Wagner, R. Kirchheim and M. Ru'hle, *Acta Metallurgica et Materialia* **1992**, 40, S85-S93.
- [134] D. Klotz, B. Butz, A. Leonide, J. Hayd, D. Gerthsen and E. Ivers-Tiffée, *Journal of The Electrochemical Society* **2011**, 158, B587.
- [135] C. Chatzichristodoulou, M. Chen, P. V. Hendriksen, T. Jacobsen and M. B. Mogensen, *Electrochimica Acta* **2016**, 189, 265-282.

- [136] M. B. Mogensen, M. Chen, H. L. Frandsen, C. R. Graves, A. Hauch, P. V. Hendriksen, T. Jacobsen, S. H. Jensen, T. L. Skaftø and X. Sun, *14th European SOFC & SOE Forum 2020* **2020**.
- [137] Y. Shang, A. L. Smitshuysen, M. Yu, Y. Liu, X. Tong, P. S. Jørgensen, L. Rorato, J. Laurencin and M. Chen, *Journal of Materials Chemistry A* **2023**, *11*, 12245-12257.
- [138] A. Nakajo, G. Rinaldi, P. Caliendo, G. Jeanmonod, L. Navratilova, M. Cantoni and J. Van herle, *Journal of Electrochemical Energy Conversion and Storage* **2020**, *17*.
- [139] B. I. Dembele, *Salt-water Electrolysis for Green Hydrogen Economy, Master thesis, WASCAL*, **2023**.
- [140] I. D. Unachukwu, V. Vibhu, J. Uecker, I. C. Vinke, R.-A. Eichel and L. B. de Haart, *Journal of CO₂ Utilization* **2023**, *69*, 102423.
- [141] S. Foit, L. Dittrich, T. Duyster, I. Vinke, R.-A. Eichel and L. G. J. de Haart, *Processes* **2020**, *8*, 1390.
- [142] V. Bilalis, X. Sun, H. L. Frandsen and M. Chen, *Journal of Power Sources* **2024**, *606*, 234490.
- [143] J. Jiang and J. L. Hertz, *Journal of Electroceramics* **2014**, *32*, 37-46.
- [144] E. Bucher, W. Sitte, I. Rom, I. Papst, W. Grogger and F. Hofer, *Solid State Ionics* **2002**, *152-153*, 417-421.
- [145] E. Konyshcheva, R. Blackley and J. T. Irvine, *Chemistry of Materials* **2010**, *22*, 4700-4711.
- [146] H. J. Avila-Paredes, K. Choi, C.-T. Chen and S. Kim, *Journal of Materials Chemistry* **2009**, *19*, 4837-4842.
- [147] S. He, Y. Zou, K. Chen and S. P. Jiang, *Interdisciplinary Materials* **2023**, *2*, 111-136.
- [148] Elcogen, *Solid oxide electrolysis cells*, **2025**, <https://elcogen.com/products/solid-oxide-electrolysis-cells/>, accessed 06.06.2025.
- [149] A. Nenning, M. Holzmann, J. Fleig and A. K. Opitz, *Materials Advances* **2021**, *2*, 5422-5431.
- [150] S. D. Ebbesen, X. Sun and M. B. Mogensen, *Faraday Discussions* **2015**, *182*, 393-422.
- [151] S. Primdahl and M. Mogensen, *Journal of The Electrochemical Society* **1999**, *146*, 2827.
- [152] A. Nenning, C. Bischof, J. Fleig, M. Bram and A. K. Opitz, *Energies* **2020**, *13*, 987.
- [153] Y. Tao, S. D. Ebbesen and M. B. Mogensen, *Journal of The Electrochemical Society* **2014**, *161*, F337.
- [154] M. Ni, *Chemical Engineering Journal* **2010**, *164*, 246-254.
- [155] M. Ni, M. K. H. Leung and D. Y. C. Leung, *Journal of Power Sources* **2006**, *163*, 460-466.
- [156] B. Königshofer, M. Höber, G. Nusev, P. Boškoski, C. Hochenauer and V. Subotić, *Journal of Power Sources* **2022**, *523*, 230982.

- [157] Y. Yang, X. Tong, A. Hauch, X. Sun, Z. Yang, S. Peng and M. Chen, *Chemical Engineering Journal* **2021**, 417, 129260.
- [158] V. Bilalis, B. Li, H. L. Frandsen and M. Chen, *ECS Transactions* **2023**, 111, 429.
- [159] S. Drvarič Talian, G. Kapun, J. Moškon, R. Dominko and M. Gaberšček, *Nature Communications* **2025**, 16, 2030.
- [160] F. El Gabaly, M. Grass, A. H. McDaniel, R. L. Farrow, M. A. Linne, Z. Hussain, H. Bluhm, Z. Liu and K. F. McCarty, *Physical Chemistry Chemical Physics* **2010**, 12, 12138-12145.
- [161] X. Song, X. Dong, M. Li and H. Wang, *Journal of Power Sources* **2016**, 308, 58-64.
- [162] L. M. Russell and E. G. Singh, *Aerosol Science and Technology* **2006**, 40, 664-671.
- [163] M. Riedel, M. P. Heddrich and K. A. Friedrich, *Fuel Cells* **2020**, 20, 592-607.
- [164] E. Chinarro, F. M. Figueiredo, G. C. Mather, J. R. Jurado and J. R. Frade, *Journal of the European Ceramic Society* **2007**, 27, 4233-4236.
- [165] N. M. Tikekar, T. J. Armstrong and A. V. Virkar, *Journal of The Electrochemical Society* **2006**, 153, A654.
- [166] T. Takeguchi, T. Yano, Y. Kani, R. Kikuchi and K. Eguchi, *ECS Proceedings Volumes* **2003**, 2003-07, 704.
- [167] J. Taubmann, H. L. Frandsen and P. Khajavi, *Ceramics International* **2024**, 50, 43108-43121.
- [168] S. Vafaeenezhad, A. R. Hanifi, M. A. Laguna-Bercero, T. H. Etsell and P. Sarkar, *Materials Futures* **2022**, 1, 042101.
- [169] F. Monaco, M. Hubert, J. Vulliet, J. Ouweltjes, P. D. Montinaro, P. Cloetens, P. Piccardo, F. Lefebvre-Joud and J. Laurencin, *Journal of The Electrochemical Society* **2019**.
- [170] M. Scimeca, A. Orlandi, I. Terrenato, S. Bischetti and E. Bonanno, *Eur J Histochem* **2014**, 58, 2403.
- [171] European Network of Forensic Science Institutes, *GUIDELINE FOR THE SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE SPECTROSCOPY OF GLASS SAMPLES IN FORENSIC SCIENCE*, **2022**.
- [172] J. Zinke, E. D. Nilsson, P. Zieger and M. E. Salter, *Journal of Geophysical Research: Atmospheres* **2022**, 127, e2021JD036005.
- [173] D. M. Murphy, K. D. Froyd, H. Bian, C. A. Brock, J. E. Dibb, J. P. DiGangi, G. Diskin, M. Dollner, A. Kupc, E. M. Scheuer, G. P. Schill, B. Weinzierl, C. J. Williamson and P. Yu, *Atmos. Chem. Phys.* **2019**, 19, 4093-4104.
- [174] M. Sokić, Ž. Kamberović, V. Nikolić, B. Marković, M. Korać, Z. Anđić and M. Gavrilovski, *The Scientific World Journal* **2015**, 2015, 601970.
- [175] S. Zhou, Y. Wei, B. Li, H. Wang, B. Ma and C. Wang, *Scientific Reports* **2016**, 6, 29061.
- [176] C. Xu, M. Gong, J. W. Zondlo, X. Liu and H. O. Finklea, *Journal of Power Sources* **2010**, 195, 2149-2158.

- [177] T. S. Li, C. Xu, T. Chen, H. Miao and W. G. Wang, *Journal of Solid State Electrochemistry* **2011**, *15*, 1077-1085.
- [178] K. Haga, Y. Shiratori, K. Ito and K. Sasaki, *Journal of The Electrochemical Society* **2008**, *155*, B1233.
- [179] L. Inkmann, *Green hydrogen from seawater: Integration of solid oxide electrolyzer cells in novel process concepts*, Master Thesis, RWTH Aachen **2023**.
- [180] A. H. Haidari, G. J. Witkamp and S. G. J. Heijman, *Water Resources and Industry* **2022**, *27*, 100171.
- [181] G. Micale, L. Rizzuti and A. Cipollina, *Seawater desalination: conventional and renewable energy processes*, Springer, **2009**.
- [182] M. Bialik, P. Sedin and H. Theliander, *Industrial & Engineering Chemistry Research* **2008**, *47*, 1283-1287.
- [183] G. Min, Y. J. Park and J. Hong, *Energy Conversion and Management* **2020**, *225*, 113381.
- [184] G. Schiller, M. Lang, P. Szabo, N. Monnerie, H. von Storch, J. Reinhold and P. Sundarraj, *Journal of Power Sources* **2019**, *416*, 72-78.
- [185] T. Bui, D. Lee, K. Y. Ahn and Y. S. Kim, *Energy Conversion and Management* **2023**, *278*, 116704.
- [186] G. Jiménez-Martín, X. Judez, M. Aguado and I. Garbayo, *International Journal of Hydrogen Energy* **2024**.
- [187] M. T. Zun and B. C. McLellan, *Hydrogen* **2023**, *4*, 932-960.
- [188] M. Gül and E. Akyüz, *Journal of Cleaner Production* **2023**, *430*, 139627.
- [189] G. Fan, H. Zhang, B. Sun and F. Pan, *Nature Communications* **2025**, *16*, 4284.
- [190] Y. Wang, Y. Ling, B. Wang, G. Zhai, G. Yang, Z. Shao, R. Xiao and T. Li, *Energy & Environmental Science* **2023**, *16*, 5721-5770.
- [191] L. Schley, V. Vibhu, L. Nohl, I. C. Vinke, L. G. J. de Haart and R.-A. Eichel, *Energy Advances* **2024**, *3*, 861-873.
- [192] K. Im-orb, N. Visitdumrongkul, D. Saebea, Y. Patcharavorachot and A. Arpornwichanop, *Journal of Cleaner Production* **2018**, *170*, 1-13.
- [193] M. Nohl, *Modellierung der Hochtemperaturelektrolyse von H₂O und CO₂*, RWTH Aachen, **2024**.
- [194] The Engineering ToolBox, *Water Thermal Properties – Density, Heat Capacity, and Conductivity*, **2003**, https://www.engineeringtoolbox.com/water-thermal-properties--d_162.html, accessed 06.05.2025.
- [195] The Engineering ToolBox, *Hydrogen - Density and Specific Weight vs. Temperature and Pressure*, **2018**, https://www.engineeringtoolbox.com/hydrogen-H2-density-specific-weight-temperature-pressure-d_2044.html, accessed 06.05.2025.

[196] Henan Lanphan Industry Co, Lanphan falling film evaporator (*Evaporation Equipment*), **2025**.

[197] Pure-Pro Water Corporation, *PurePro USA Industrial Reverse Osmosis System.*, **2025**.

9 Appendix

9.1 Tables

Table A 1 Salt ion content in the used seawater analyzed by ICP-OES.

Ingredient	Concentration (mg/L)
Na	9740
Mg	1163
K	402
Ca	337
Cl	16968
SO ₄	2333
Br	59

Table A 2 Used cells for the stability tests with the corresponding production batch.

Name of measured cell	Production batch
Pure water cell 1	Old
Pure water cell 2	Old
Pure water cell 3	Old
Pure water cell 4	New
Pure water cell 5	New
Seawater 1	New
NaCl 1	Old

Table A 3 Balance of plant components and the corresponding efficiencies ^[98-99].

Balance of plant component	Efficiency (%)
Water pump	70
Compressor	75
Electric heater	98
Heat exchangers	95
AC/DC converter	95

Table A 4 SWRO system operation parameters.

Parameter	Value
Recovery (%)	40
Salt Rejection (%)	99
Installed Power (kW)	42
Supplied Feed Pressure (bar)	5.5

Table A 5 Overview of input parameters for the techno economic analysis.

Parameter	Symbol	Value	Unit	Source
Electrical Power	P_{el}	1	MW	-
Gibbs Energy	ΔG_f	188.635	kJ/mol	-
Current density	J	10000	A/m ²	[99]
Pre-exponential factor for anode exchange current density	γ_a	$2.051 \cdot 10^9$	A/m ²	[192]
Pre-exponential factor for cathode exchange current density	γ_c	$1.344 \cdot 10^{10}$	A/m ²	[192]
Activation energy for the anode	$E_{act,a}$	120	kJ/mol	[192]
Activation energy for the cathode	$E_{act,c}$	100	kJ/mol	[192]
Thickness of the cathode	d_c	300	μm	[148]
Thickness of the electrolyte	d_e	3	μm	[148]
Thickness of the anode	d_a	15	μm	[148]
Porosity of the anode	ϵ_a	0.43	-	[193]
Porosity of the cathode	ϵ_c	0.265	-	[193]
Tortuosity of the anode	τ_a	1.5	-	[193]
Tortuosity of the cathode	τ_c	4.5	-	[193]
Average pore radius	r	0.5	μm	[99]
Effective diffusion coefficient for H ₂ O	$D_{eff}^{H_2O}$	$1.6857 \cdot 10^{-5}$	m ² /s	-
Specific heat capacity of water vapor	C_{p, H_2O}	1.996	kJ/kg·K	[194]
Specific heat capacity of hydrogen	C_{p, H_2}	14.31	kJ/kg·K	[195]
Specific heat capacity of oxygen	C_{p, O_2}	0.92	kJ/kg·K	[195]
Efficiency of the current transformer	η_{CT}	0.95	-	[99]
Steam utilization factor	U	0.85	-	[99]
Proportion of O ₂ on the anode side	x_{O_2}	1	-	-
Universal gas constant	R	8.314	J/mol·K	-
Faraday constant	F	96485	C/mol	-

Table A 6 Summary of the CAPEX for the FFE case ^[109, 196].

CAPEX	Cost (USD)
SOEC stack	520000.00
Power supply	198225.00
Steam/Water Circulation	66400.00
Hydrogen processing	106580.00
Cooling/Heat exchange	84000.00
Electric Heater	5000.00
FFE	20000.00
Other BOPs	6000.00
Total	1006205.00

Table A 7 Component costs for the FFE case ^[109, 196].

Description	Component	Cost (\$/unit)
SOEC	SOEC	520000.00
Circulation	Circulation pump	5500.00
	Compressor	11400.00
	Piping	7600.00
	Valves, Control	7700.00
	Dryer	13900.00
Hydrogen processing	Hydrogen Separator	28000.00
	Tubing	3800.00
	Valves, Control	5200.00
Cooling/Heating	Heat Exchanger	9000.00
	Valves, Control	3000.00
FFE	FFE	20000.00
Other BOPs	Other BOPs	6000.00

Table A 8 Summary of the CAPEX for the SWRO case ^[109, 197].

CAPEX	Cost (USD)
SOEC stack	520000.00
Power supply	198225.00
Steam/Water Circulation	66400.00
Hydrogen processing	106580.00
Cooling/Heat exchange	66000.00
Electric Heater	5000.00
SWRO unit	21400.00
Other BOPs	6000.00
Total	989605.00

Table A 9 Component costs for the SWRO case ^[109, 197].

Description	Component	Cost (\$/unit)
SOEC	SOEC	520000.00
Circulation	Circulation pump	5500.00
	Compressor	11400.00
	Piping	7600.00
	Valves, Control	7700.00
	Dryer	13900.00
Hydrogen processing	Hydrogen Separator	28000.00
	Tubing	3800.00
	Valves, Control	5200.00
Cooling/Heating	Heat Exchanger	9000.00
	Valves, Control	3000.00
SWRO unit	SWRO unit	21400.00
Other BOPs	Other BOPs	6000.00

Table A 10 Theoretical and experimental determined OCV values for cells operated with steam from seawater with a variation of operating temperature at constant gas compositions of 60 % H₂O + 40 % H₂.

Temperature	OCV theo.	OCV Cell A	OCV Cell B	OCV Cell C
900	0.890	0.899	0.890	0.896
875	0.899	0.907	0.897	0.905
850	0.908	0.914	0.910	0.914
825	0.917	0.927	0.916	0.925
800	0.925	0.934	0.925	0.934
775	0.933	0.941	0.933	0.943
750	0.941	0.950	0.943	0.948

Table A 11 Theoretical and experimental determined OCV values for cells operated with steam from seawater with a variation of steam contents at the fuel electrode at 800 °C.

Gas composition	OCV theo.	OCV Cell D	OCV Cell E
60% H ₂ O	0.925	0.925	0.926
50% H ₂ O	0.944	0.941	0.933
40% H ₂ O	0.952	0.960	0.950
30% H ₂ O	0.983	0.977	0.970
20% H ₂ O	1.008	0.998	0.995
10% H ₂ O	1.045	1.034	1.030

Table A 12 Theoretical and experimental determined OCV values for cells operated with steam from saturated sodium chloride solution with a variation of operating temperature at constant gas compositions of 60 % H₂O + 40 % H₂.

Temperature	OCV theo.	OCV Cell NaCl
900	0.890	0.901
875	0.899	0.910
850	0.908	0.923
825	0.917	0.930
800	0.925	0.940
775	0.933	0.947
750	0.941	0.956

Table A 13 Theoretical and experimental determined OCV values for cells operated with steam from saturated sodium chloride solution with a variation of steam contents at the fuel electrode at 800 °C.

Gas composition	OCV theo.	OCV Cell NaCl
60 % H ₂ O + 40 % H ₂	0.925	0.926
50 % H ₂ O + 50 % H ₂	0.944	0.940
40 % H ₂ O + 60 % H ₂	0.952	0.959
30 % H ₂ O + 70 % H ₂	0.983	0.976
20 % H ₂ O + 80 % H ₂	1.008	0.998
10 % H ₂ O+ 90 % H ₂	1.045	1.030

9.2 Figures

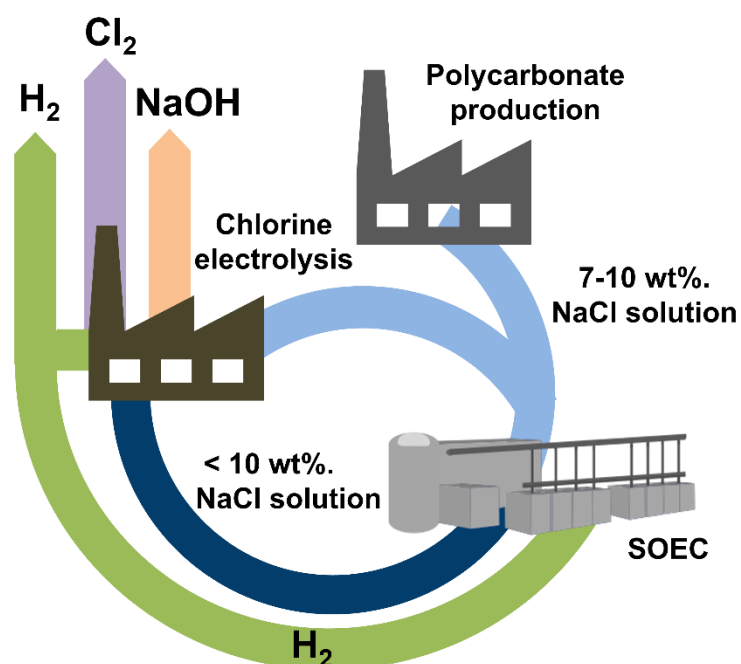


Figure A 1 Concept for the utilization of wastewater in a circular approach in the SOEC system to produce hydrogen from wastewater.

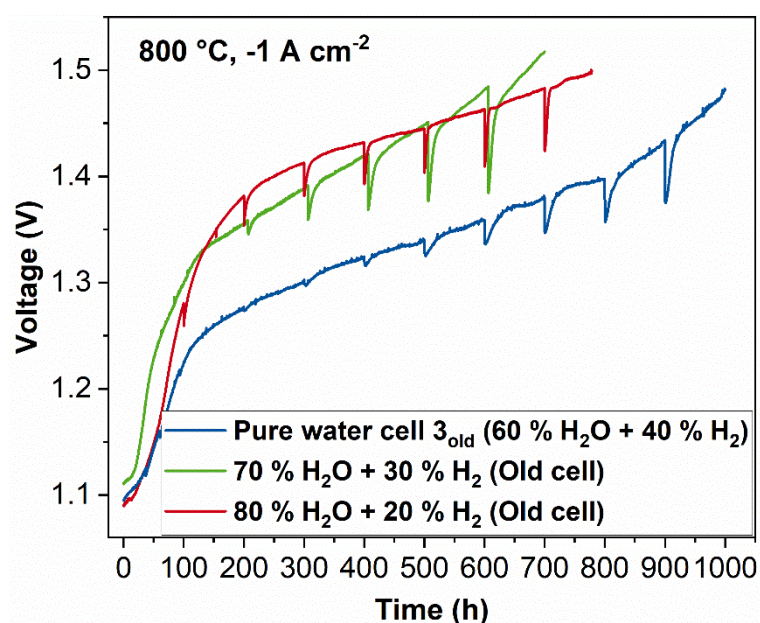


Figure A 2 (a) Cell Voltage evolution of SOEC cells from the old production batch at different steam content.

Pure water cell 3_{old}

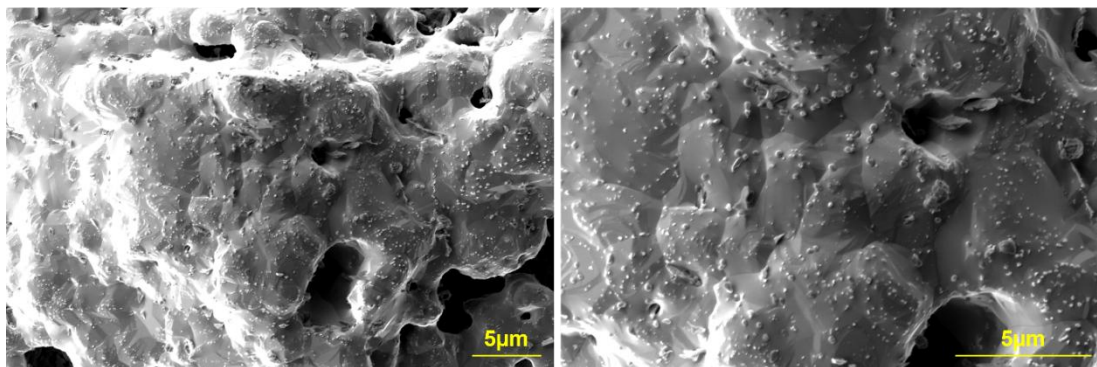


Figure A 3 SEM images of the Ni-YSZ fuel electrode surface after operation for 1000 hours with pure water.

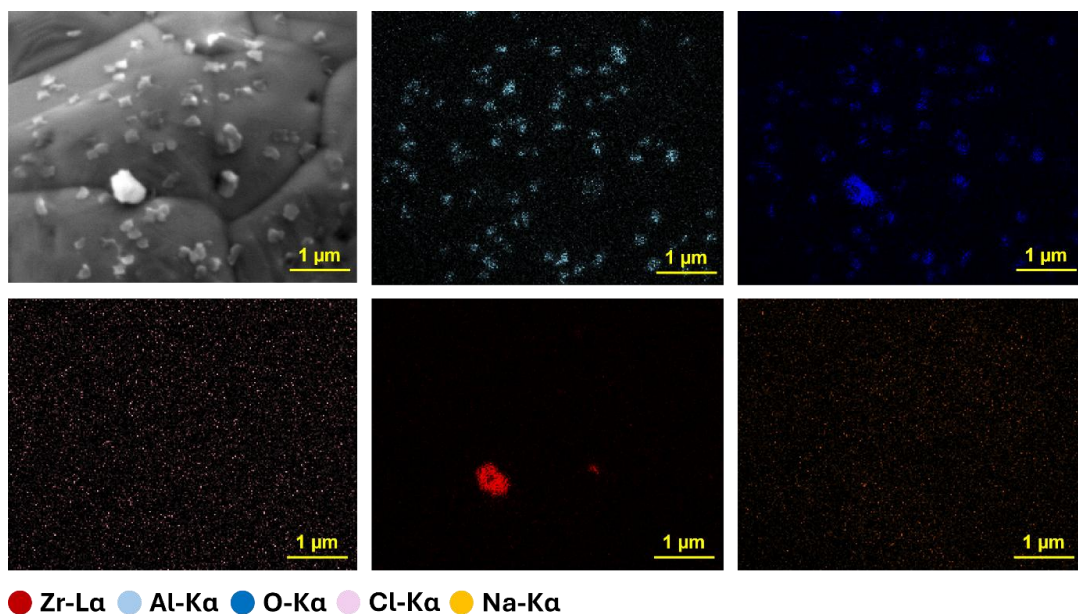


Figure A 4 SEM-EDX analysis of the Ni-YSZ fuel electrode surface of seawater cell 1_{new} after 1000 hours of operation.

Seawater cell 1_{new}

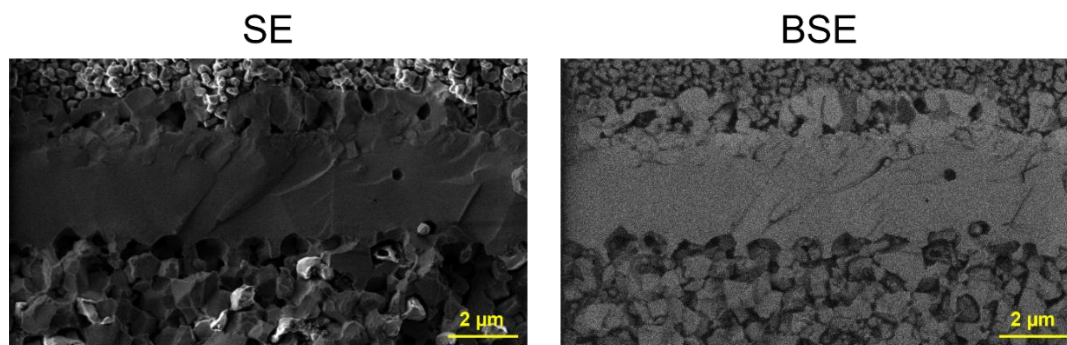


Figure A 5 SEM images of the fractured cross section of seawater cell 1_{new} after 1000 hours of operation.

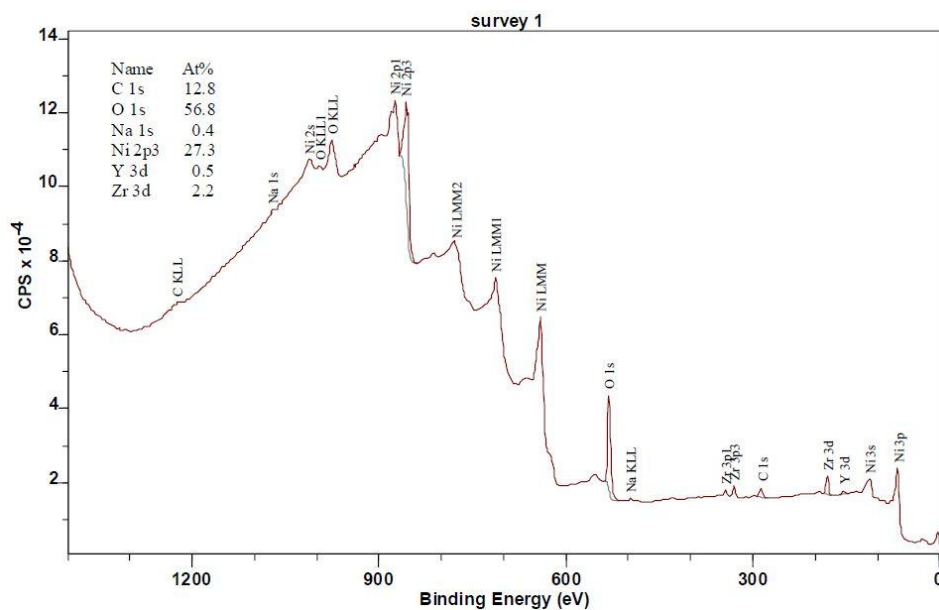


Figure A 6 XPS spectra of the fuel electrode surface of the degraded pure water cell 3_{old} at room temperature and after disassembly.

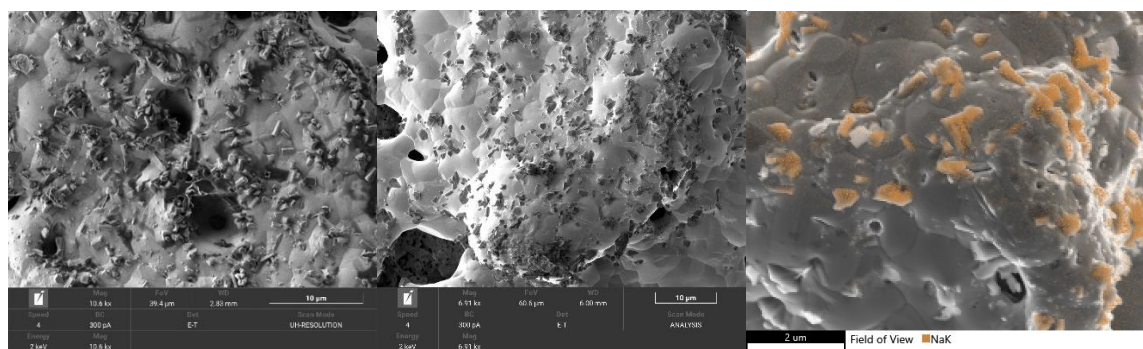
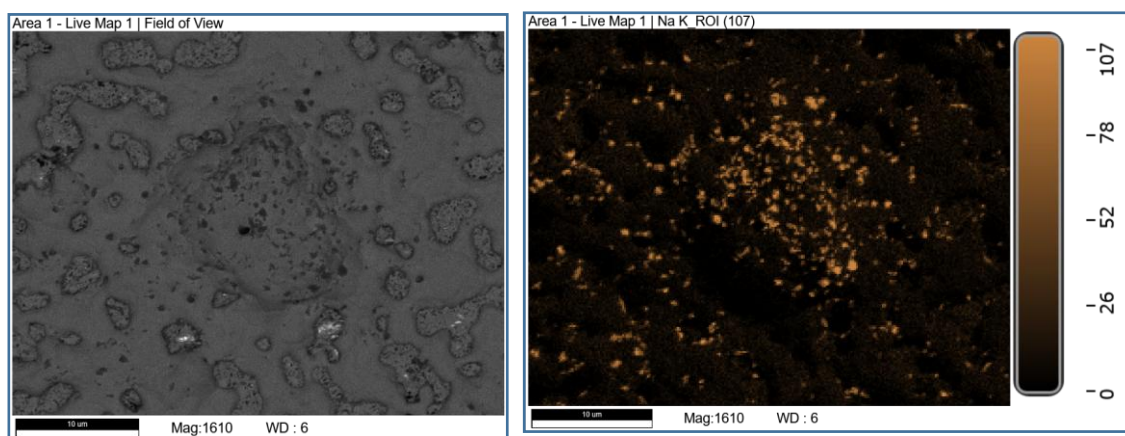


Figure A 7 Several spots showing SEM-EDX analysis of the Ni-YSZ surface of the NaCl cell 1_{old} after operation.

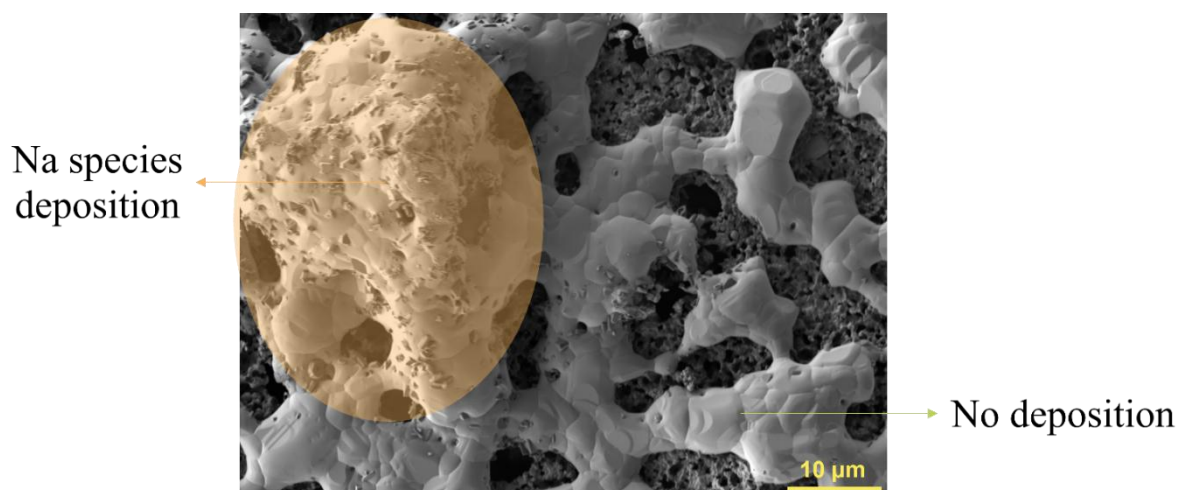
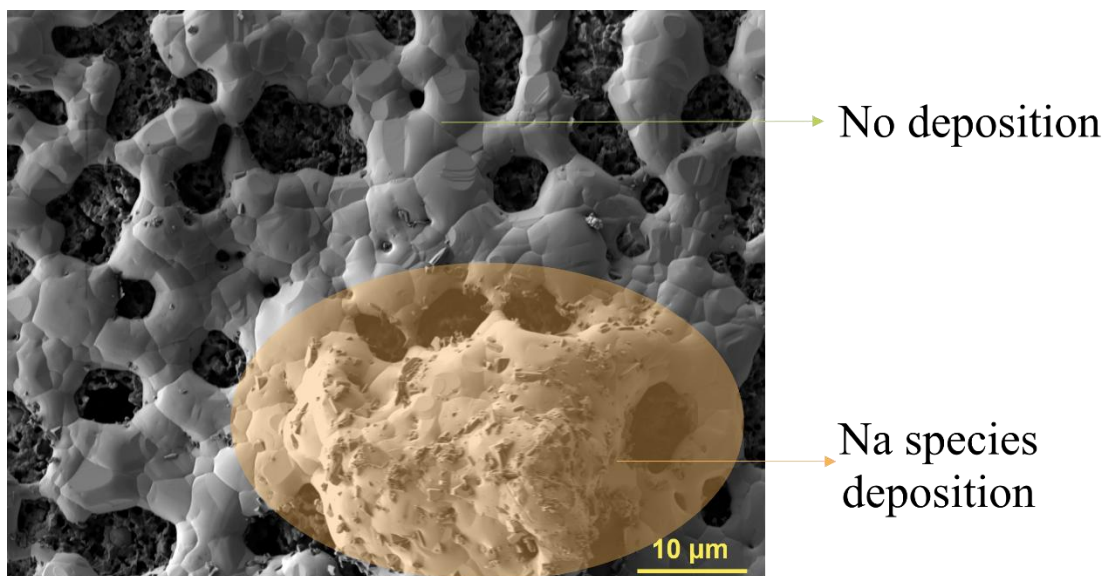
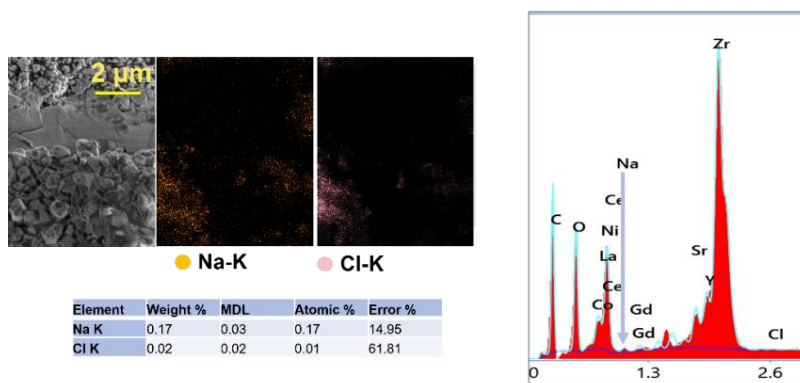
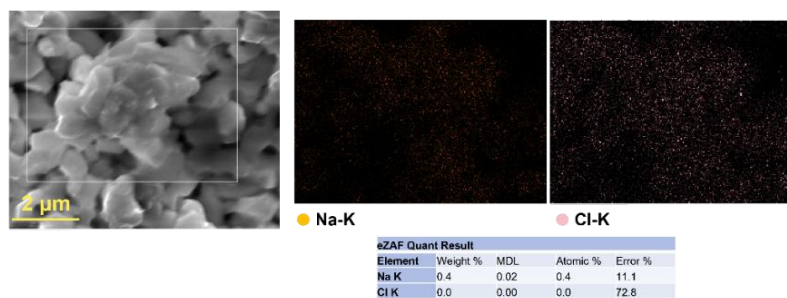


Figure A 8 SEM images of the Ni contact layer on top of the Ni-YSZ fuel electrode of NaCl cell 1_{old} after operation. Sodium species deposition is found on “hills” in the contact layer structure marked with orange circles.

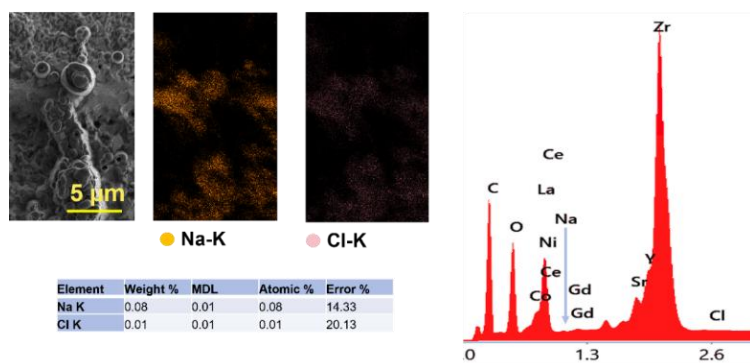
EDX Map Measurement 1: Fractured cross section of Ni-YSZ/YSZ/GDC/LSC



EDX Map Measurement 2: Fractured cross section of Ni-YSZ AFL



EDX Map Measurement 3: Fractured cross section of Ni-YSZ/YSZ/GDC/LSC



EDX Map Measurement 4: FIB-cutted cross section of Ni-YSZ support

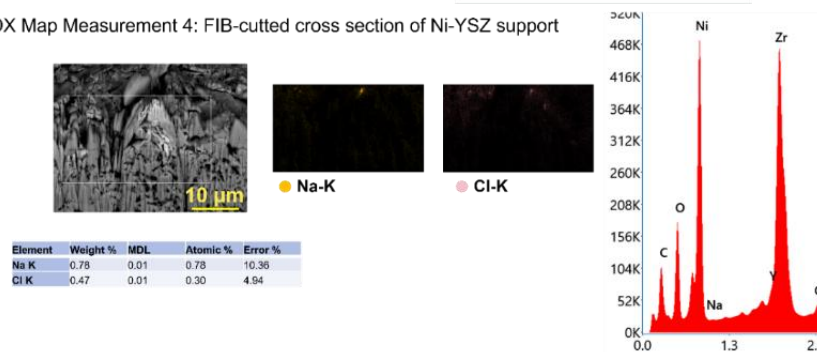
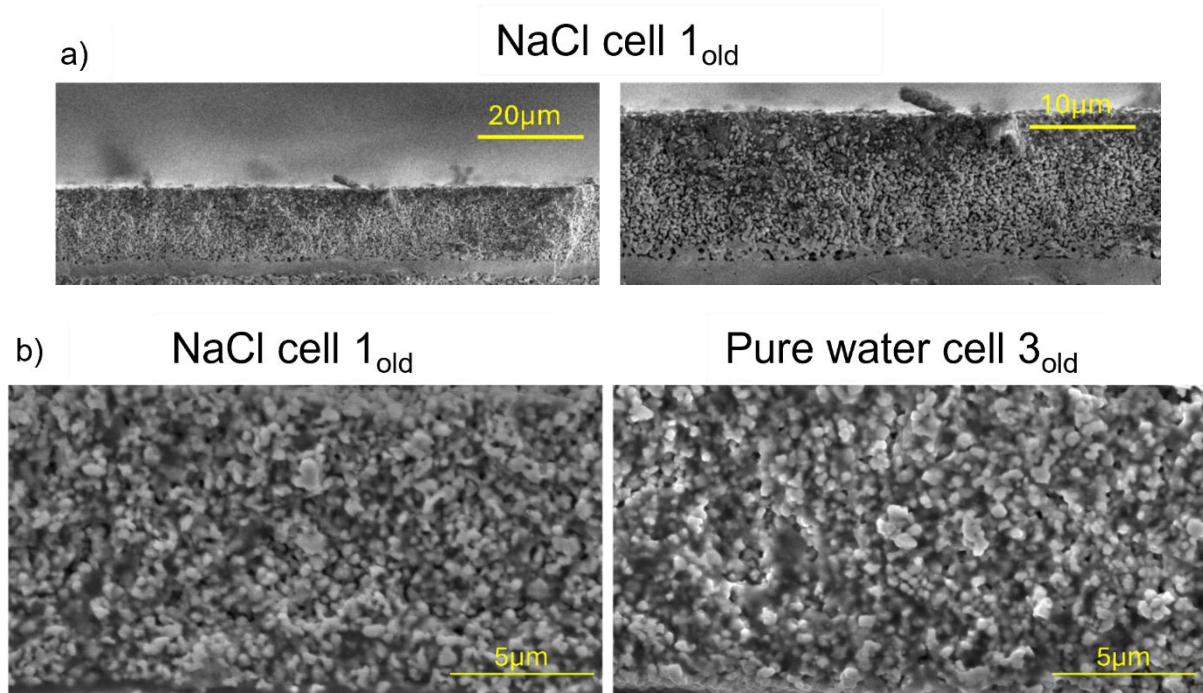


Figure A 9 EDX measurements of different location in the Ni-YSZ fuel electrode cross section of NaCl cell 1_{old} after operation to detect Na containing salt depositions.



S

Figure A 10 a) Fractured cross section of the NaCl operated cell with no delamination occurring for both electrodes and b) SEM images of the polished cross section of the air electrode for NaCl cell 1_{old} and pure water cell 3_{old}.

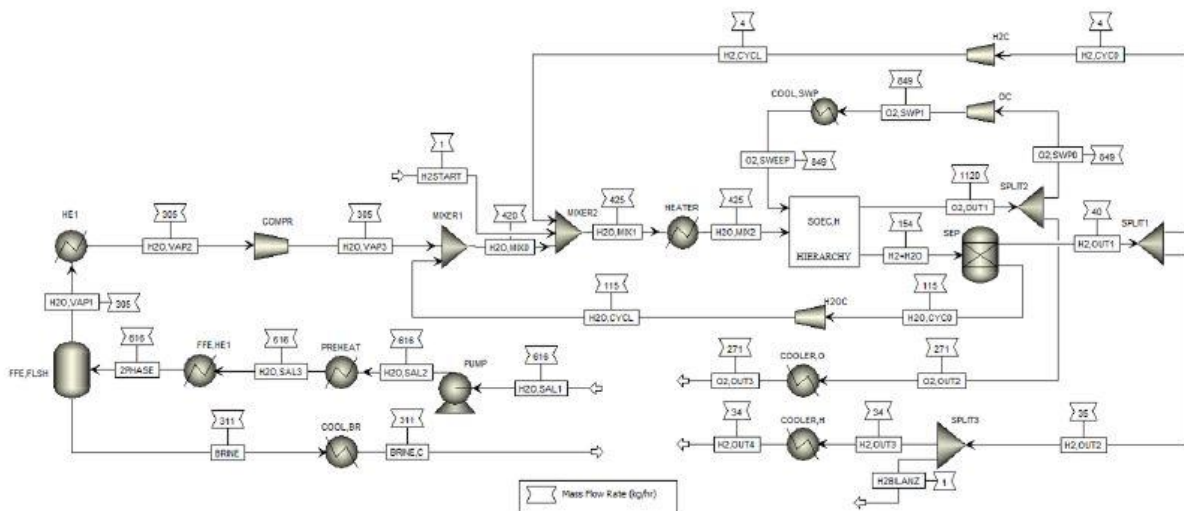


Figure A 11 Developed Aspen optimized flowsheet for the FFE/SOEC case.

9.3 Publications, Patents and Conference Contributions

9.3.1 Publications

- **Internal Biogas Reforming in Solid Oxide and Proton Conducting Ceramic Cells: Progress, Challenges and Perspectives**

S.E. Wolf, Jan Uecker, Niklas Eyckeler, Leon Schley, L.G.J. (Bert) de Haart, Vaibhav Vibhu, Rüdiger-A. Eichel

Journal of Physics: Energy, 2025, 7, 021002

Contribution: I initiated the writing process and wrote the section about challenges and strategies.

- **The utilization of high saline sodium chloride containing waters in solid oxide electrolyzers**

Jan Uecker, Lucy Nohl, Vaibhav Vibhu, Jean-Pierre Poc, Pritam Chakraborty, Izaak C. Vinke, Shibabrata Basak, L.G.J.(Bert) de Haart, Rüdiger-A. Eichel

Journal of Power Sources, 2025, 633, 236390

Contribution: I was the main author of the publication and performed the presented electrochemical results and the analysis.

- **Impact of Electrochemical Impedance Spectroscopy Dataset Curation on Solid Oxide Cell Degradation Assessment**

Christian Mänken, Jan Uecker, Dominik Schäfer, L. G. J. (Bert) de Haart and Rüdiger-A. Eichel

Journal of the Electrochemical Society, 2024, 171, 064503

Contribution: Experimental data and analysis of single cell measurements, comparison with commercial software, writing of the single cell part and proofreading.

- **Gadolinium Doped Ceria as Nickel-Free Fuel Electrode in High Temperature CO₂-Electrolysis**

Jan Uecker, Ifeanyichukwu D. Unachukwu, Vaibhav Vibhu, Izaak C. Vinke, L. G. J. (Bert) de Haart, and Rüdiger-A. Eichel

ChemElectroChem, 2024, 11, e202300617

Contribution: I was the main author of the paper and performed the presented results and the analysis.

- **Performance, electrochemical process analysis and degradation of gadolinium doped ceria as fuel electrode material for solid oxide electrolysis cells**

Jan Uecker, Ifeanyichukwu D. Unachukwu, Vaibhav Vibhu, Izaak C. Vinke, Rüdiger-A. Eichel, L.G.J. (Bert) de Haart

Electrochimica Acta, 2023, 452, 1432320

Contribution: I was the main author of the paper and performed the presented results and analysis.

- **Electrochemical impedance analysis and degradation behavior of a Ni-GDC fuel electrode containing single cell in direct CO₂ electrolysis**

Ifeanyichukwu D. Unachukwu, Vaibhav Vibhu, Jan Uecker, Izaak C. Vinke, Rüdiger-A. Eichel, L.G.J. (Bert) de Haart

Journal of CO₂ Utilization, 2023, 69, 102423

Contribution: I helped with the electrochemical analysis and measurement of the electrochemical results.

- **Comparison of the Electrochemical and Degradation Behaviour of Ni-YSZ and Ni-GDC Electrodes Under Steam, Co- and CO₂ Electrolysis**

Ifeanyichukwu D. Unachukwu, Vaibhav Vibhu, Jan Uecker, Izaak C. Vinke, Rüdiger-A. Eichel, and L.G.J. (Bert) de Haart

ECS Transactions, 2023, 111 (6) 1445-1452

Contribution: I performed the measurements and analysis of the electrochemical data of the Ni-GDC cells in CO₂ electrolysis conditions.

- **Electrochemical Activity and Stability of Pure Gadolinium Doped Ceria as Fuel Electrode in Solid Oxide Electrolysis Cells**

J. Uecker, I.D. Unachukwu, V. Vibhu, I.C. Vinke, R.-A. Eichel, and L.G.J. (Bert) de Haart

ECS Transactions, 2023, 111 (6) 1785-1793

Contribution: I was the main author of the manuscript. I performed all shown experiments and analysis of the data.

9.3.2 Patents

- **Filing: Solid oxide cell with nickel free fuel electrode**

2023, German Patent Office

2024, European Patent Office

9.3.3 Conference Oral and Poster Contributions

Self-applied and not self-presented:

- **Oral (presented by Dr. Till Frömling): Seawater Utilization in Solid Oxide Electrolysis Cells: A Scientific, Technical and Economic Evaluation**

J. Uecker, V. Vibhu, I. Vinke, T. Frömling, L. Inkmann, M. Wehner, R. Keller, M. Wessling, L.G.J. (Bert) de Haart and R.A.-Eichel

19th International Symposium on Solid Oxide Fuel Cells (SOFC-XIX), July 2025, Stockholm, Sweden.

Self-applied and self-presented:

- **Oral: Direct Use of European Seawater in Solid Oxide Electrolysis Cells**

J. Uecker, B.I. Dembele, L. Nohl, N. Eyckeler, V. Vibhu, I. Vinke, L.G.J. (Bert) de Haart and R.A.-Eichel

16th European SOFC and SOE Forum, 2 – 5 July 2024, Luzern Switzerland.

- **Poster: The Utilization of Sodium Chloride Concentrated Wastewaters in Solid Oxide Electrolysis Cells**

J. Uecker, L. Nohl, V. Vibhu, I. Vinke, L.G.J. (Bert) de Haart and R.A.-Eichel

16th European SOFC and SOE Forum, 2 – 5 July 2024, Luzern Switzerland.

- **Poster: Direct Internal Dry Reforming of a CH₄/CO₂ gas mixture in Solid Oxide Cells**

L. Nohl, J. Uecker, C. Li, M. Nohl, V. Vibhu, I. Vinke, L.G.J. (Bert) de Haart and R.A.-Eichel

16th European SOFC and SOE Forum, 2 – 5 July 2024, Luzern Switzerland.

- **Oral: Electrochemical Activity and Stability of Pure Gadolinium Doped Ceria as Fuel Electrode in Solid Oxide Electrolysis Cells**

J. Uecker, I.D. Unachukwu, V. Vibhu, I.C. Vinke, R.-A. Eichel, and L.G.J. (Bert) de Haart

18th International Symposium on Solid Oxide Fuel Cells (SOFC-XVIII), June 2023, Boston USA.

9.4 Figure Directory

Figure 1 Representation of a reversible and flexible operatable SOC system.....	3
Figure 2 Schematic representation of the working principle of a SOC operated in SOFC and SOEC mode in a H ₂ /H ₂ O system.....	4
Figure 3 Illustration of the total energy demand, heat demand and electricity demand based on thermodynamics of water electrolysis with typical ranges of cell voltages taken from ^[20] . .	6
Figure 4 Typical voltage ranges as a function of current density for water electrolysis of low temperature and high temperature cells taken from ^[22]	6
Figure 5 Degradation mechanisms occurring in Ni-YSZ fuel electrodes during SOEC operation.	7
Figure 6 Nyquist plot including three individual three individual time constants and description of the ohmic and polarization resistance.....	13
Figure 7 Exemplary circuit model referring to processes occurring in a SOC system.....	14
Figure 8 Freshwater demand in Germany in 2023 and the expected needed freshwater demand for hydrogen production equal to 600 TWh/year by 2025. The figure is based on ^[73]	20
Figure 9 Graphical representation of the thesis research and development with the research questions.....	23
Figure 10 Schematic illustration of the used measurement setup.	25
Figure 11 Schematic representation of the used Ni-YSZ fuel electrode single cell with a total diameter of 2 cm.....	26
Figure 12 Voltage time plots of individual Ni-YSZ fuel electrode supported cells with steam produced from pure water.	37
Figure 13 iV characteristics recorded every 100 hours during the stability test for (a) a cell from the old production batch and (b) the new production batch. Comparison of the evolution in (c) ASR values at OCV and (d) the current density at 1.4 V for the old and new production batch.	40
Figure 14 Nyquist plots and DRT spectra derived from EIS data recorded every 100 hours during the stability test for (a, b) a cell from the old production batch and (c, d) the new production batch.....	42
Figure 15 (a) Comparison of DRT plots of measured and fitted data, (b) comparison of Nyquist plot of measured and fitted data with the individual contribution of the 4 RQ ECM model, (c) absolute residuals and (d) relative residuals of the ECM fit in a gas composition of 60 % H ₂ O + 40 % H ₂ at 800 °C and OCV.	43
Figure 16 Evolution of the (a) R _Ω , (b) R _p and the individual resistances of the processes (c, d) for a cell from the old production and a cell from the new production batch. All data shown is	

derived from the ECM fitting of the EIS data recorded every 100 hours during the stability measurement at OCV.....	44
Figure 17 Evolution of the R_{Ω} , the resistance corresponding to the Ni-YSZ fuel electrode and the resistance corresponding to the air electrode for (a) a cell from the old production and (b) a cell from the new production batch.	46
Figure 18 SEM images of the fractured cross section of the electrolyte/Ni-YSZ electrode active area interface for a pristine reduced, pure water cell 3 _{old} from the old production batch and pure water cell 4 _{new} from the new production batch.	47
Figure 19 (a) SEM images showing the embedded and polished cross section of the Ni-YSZ electrode active layer of a pristine reduced cell, pure water cell 3 _{old} from the old production batch and pure water cell 4 _{new} from the new production batch. Red arrows indicate gaps between the Ni and YSZ phases, while red squares mark inclusions within the Ni particles. (b) SEM-EDX analysis of a Ni particle in the Ni-YSZ active layer of pure water cell 3 _{old}	48
Figure 20 SEM-EDX analysis of the Ni-YSZ fuel electrode of a pristine reduced cell, pure water cell 3 _{old} from the old production batch and pure water cell 4 _{new} from the new production batch.	49
Figure 21 iV curves of three individual (A, B, C) Ni-YSZ fuel electrode supported cells operated with steam produced from seawater at different operating temperatures in a gas composition of 60 % H ₂ O + 40 % H ₂	53
Figure 22 iV curves of two individual (Cell D _{new} and Cell E _{new}) Ni-YSZ fuel electrode supported cells operated with steam produced from seawater at different steam contents with H ₂ as balance gas at a constant temperature of 800 °C.	55
Figure 23 Comparison of individual Ni-YSZ fuel electrode supported cells operated with steam produced from seawater and pure water as (a) iV curves at 800 °C in 60 % H ₂ O + 40 % H ₂ , (b) current densities at 1.4 V in 60 % H ₂ O + 40 % H ₂ at different operating temperatures and (c) current densities at 1.4 V and 800 °C for different steam contents with H ₂ as balance gas...56	56
Figure 24 Arrhenius plots of two seawater operated cells with (a), (b) a separate linear fit for the calculation of two activation energies for the temperature ranges 750 to 825 °C and 850 to 900 °C and (c), (d) fitting the data to a model taking account a constant gas concentration contribution to calculate the activation energy at OCV and an electrolysis current of -0.5 A·cm ⁻²	58
Figure 25 (a) Short time current density against time curves at 850 °C, 800 °C and 750 °C at a constant voltage of 1.25 V in a gas composition of 60 % H ₂ O + 40 % H ₂ with steam produced from seawater and (b) the corresponding evolution of the ohmic and polarization resistance.	61
Figure 26 (a) Short time current density against time curves at different steam contents of 60 %, 50 % and 40 % with H ₂ as balance gas at a constant voltage of 1.25 V and a temperature	

of 800 °C with steam produced from seawater and (b) the corresponding evolution of the ohmic and polarization resistance	62
Figure 27 Voltage evolution over time for cells operated with steam generated from seawater (green) and pure water (blue) at a constant current density of $-1 \text{ A}\cdot\text{cm}^{-2}$, a temperature of 800 °C and a gas composition of 60 % H_2O + 40 % H_2	63
Figure 28 iV curves recorded every 100 hours of operation (a) of pure water cell 4 _{new} operated for 1000 hours and (b) of seawater cell 1 _{new} operated for 1000 hours. Evaluation of the (c) ASR at OCV and (d) the current density at 1.4 V for both cells.	65
Figure 29 Nyquist plots and DRT spectra of the EIS data recorded at OCV every 100 hours during the stability test for (a, b) pure water cell 4 _{new} and (c, d) seawater cell 1 _{new} operated for 1000 hours.	67
Figure 30 Evolution of (a) the ohmic resistance and (b) the polarization resistance for cells operated with steam generated from seawater and pure water and the evolution of the individual process resistances for the (c) seawater cell 1 _{new} and (d) pure water cell 4 _{new} . All data shown is derived from the ECM fitting of the EIS data recorded every 100 hours during the stability measurement at OCV.	68
Figure 31 Evolution of the R_Ω , the resistance corresponding to the Ni-YSZ fuel electrode and the resistance corresponding to the LSC air electrode for (a) seawater cell 1 _{new} and (b) pure water cell 4 _{new}	70
Figure 32 (a) XRD spectra and (b) GI-XRD spectra of the Ni-YSZ fuel electrode surface of the pure water cell 4 _{new} and seawater cell 1 _{new} . Both cells were characterized after disassembly from the measurement setup and exposure to air at room temperature.	71
Figure 33 Top view of a Ni-YSZ fuel electrode surface of seawater cell 1 _{new} operated for 1000 hours with steam produced from seawater.	72
Figure 34 SEM-EDX analysis of the Ni-YSZ fuel electrode surface of seawater cell 1 _{new} operated for 1000 hours with steam produced from seawater.	73
Figure 35 SEM images of the fractured Ni-YSZ fuel electrode cross section of a pristine reduced, a cell operated for 1000 hours with pure water for steam generation, and a cell operated for 1000 hours with seawater for steam generation.	74
Figure 36 SEM-EDX maps of the Ni-YSZ fuel electrode fractured cross section of seawater cell 1 _{new} (spot 1) operated with steam generated from seawater for 1000 hours.	75
Figure 37 SEM-EDX maps of the Ni-YSZ fuel electrode fractured cross section of seawater cell 1 _{new} (spot 2) operated with steam generated from seawater for 1000 hours.	75
Figure 38 SEM images showing the embedded and polished cross section of the Ni-YSZ electrode of a pristine reduced cell, pure water cell 4 _{new} and seawater cell 1 _{new} . Red arrows indicate gaps between the Ni and YSZ phases, while red squares mark inclusions within the	

Ni particles. (b) SEM-EDX analysis of a Ni particle in the Ni-YSZ active layer of seawater cell 1 _{new} .	77
Figure 39 SEM-EDX analysis of the Ni-YSZ fuel electrode of a pristine reduced cell, pure water cell 4 _{new} and seawater cell 1 _{new} operated for 1000 hours in steam electrolysis mode.	78
Figure 40 iV curves recorded at (a) different temperatures and constant gas compositions of 60 % H ₂ O + 40 % H ₂ at the fuel electrode and (b) at different steam contents and a constant temperature of 800 °C. (c) Current densities at 1.4 V at 800 °C and 60 % H ₂ O + 40 % H ₂ in comparison with pure water reference measurements. (d) Evaluation of the activation energy of the NaCl operated cell.	83
Figure 41 (a) Voltage and (b) degradation rate evolution over time for cells operated with steam generated from saturated NaCl solution (red) and pure water (blue) at a constant current density of $-1 \text{ A}\cdot\text{cm}^{-2}$, a temperature of 800 °C and a gas composition of 60 % H ₂ + 40 % H ₂ O.	84
Figure 42 iV curves recorded every 100 hours of operation for (a) pure water cell 3 _{old} and (b) NaCl cell 1 _{old} during the stability test and the corresponding evolution of (c) the ASR at OCV and (d) the current density at 1.4 V.	86
Figure 43 Nyquist plots as a function of operation time for the (a) NaCl cell 1 _{old} and (b) the pure water cell 3 _{old} .	87
Figure 44 Evolution of the ohmic and polarization resistance during the stability test comparing the utilization of steam produced from pure water and NaCl solution. The values are derived from the EIS measurements in a gas composition of 60 % H ₂ O + 40 % H ₂ at 800 °C and OCV.	89
Figure 45 Individual resistance analysis derived from ECM fitting for the (a) NaCl cell 1 _{old} and the (b) pure water cell 3 _{old} . Corresponding DRT plots as a function of operation time for (c) the NaCl cell 1 _{old} and (d) the pure water cell 3 _{old} . Data is derived from EIS measurements at 800 °C and OCV with a gas composition of 60 % H ₂ O + 40 % H ₂ conducted every 100 hours of operation.	90
Figure 46 (a) XRD spectra and (b) GI-XRD spectra of the Ni-YSZ fuel electrode surface of pure water cell 3 _{old} and NaCl cell 1 _{old} . Both cells were characterized after disassembly out of the measurement setup and exposure to air at room temperature.	92
Figure 47 XPS spectrum of the Ni-YSZ fuel electrode surface of NaCl cell 1 _{old} at room temperature.	93
Figure 48 SEM images including SE, BSE and EDX maps of the fuel electrode surface of the NaCl operated cell.	93
Figure 49 Schematic visualization of the non uniform deposited salt particles on “islands” on the Ni-YSZ fuel electrode surface.	94

Figure 50 SEM images of the fractured Ni-YSZ fuel electrode AFL of the NaCl operated and pure water operated cell.	95
Figure 51 EDX mapping of the fractured Ni-YSZ fuel electrode active function layer of NaCl cell 1 _{old}	96
Figure 52 SEM images show the embedded and polished cross section of the Ni-YSZ electrode of a pristine reduced cell, pure water cell 3 _{old} and the NaCl cell 1 _{old} . Red arrows indicate gaps between the Ni and YSZ phases, while red squares mark inclusions within the Ni particles.	97
Figure 53 SEM and EDX maps of the Ni and Zr phase of the polished cross section of the Ni-YSZ fuel electrode of a pristine reduced, the NaCl cell 1 _{old} and pure water cell 3 _{old}	98
Figure 54 Simplified flowsheets of seawater utilization in SOEC systems for (a) the FFE and (b) the SWRO case.	101
Figure 55 (a) Composite curves showing the enthalpy requirements for seawater evaporation in the two process cases. (b) Comparison of the required enthalpy with the waste heat potential of the outgoing hot streams.	102
Figure 56 Electricity demand of the FFE/SOEC case and the SRWO/SOEC case for the direct utilization of seawater.	104
Figure 57 (a) LCOH values in SOEC system operated with fresh water and the two cases for seawater utilization. (b) Breakdown of the annualized OPEX and CAPEX for the FFE/SOEC case per year.	106
Figure 58 Sensitivity analysis of (a) the electricity price, (b) the external heating costs and (c) the freshwater price for both investigated seawater cases and the freshwater operating system.	107

9.5 Table Directory

Table 1 Processes and their assignment from literature sources for Ni-YSZ based fuel electrode supported SOCs at an oxygen content of 21 % at the air electrode.	16
Table 2 Reduction procedure with respective flow rate at fuel and air electrode.	27
Table 3 Degradation rates of the cell operated with steam produced from pure water.	38
Table 4 Quantitative analysis using the SEM/EDX images for the active functional layer and support layer of the Ni-YSZ fuel electrode.	50
Table 5 Calculated activation energies and the gas concentration resistance from a model taking into account a constant gas concentration contribution in the temperature range from 750 to 900 °C for two cells operated with steam from seawater and three cells operated in pure water conditions at OCV and $-0.5 \text{ A}\cdot\text{cm}^{-2}$ electrolysis current.	59

Table 6 Degradation values and initial voltages of individual cells operated with steam generated from seawater and pure water with different operation times.	64
Table 7 Quantitative analysis using the SEM/EDX images for the active functional layer and support layer of the Ni-YSZ fuel electrode.	79
Table 8 Degradation rate in absolute numbers every 100 hours of operation time for the utilization of saturated NaCl solution compared to pure water operation.	85
Table 9 Quantitative analysis using the SEM and EDX images for the active functional layer and support layer of the Ni-YSZ fuel electrode.	100