

Electrochemical and Microstructural Degradation and Modeling of Ni/GDC Anodes in Solid Oxide Fuel Cells

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Declaration

I declare that this dissertation is entirely my own work. Grammarly was used solely as an assistive tool for correcting grammar and typographical errors. The other content, analysis, and conclusions presented in this document are my own.

Kurzfassung

SOFCs zeigen Potenzial sowohl für stationäre als auch für mobile Energieanwendungen. Die Forschung konzentriert sich auf die Verbesserung von Leistung, Lebensdauer und Kosten. Für stationäre Systeme wie Wärme- und Stromgeneratoren wird eine Lebensdauer von 40.000–80.000 Stunden erwartet (14), obwohl konventionelle Langzeittests kostspielig und unpraktisch sind. Diese Arbeit adressiert diese Herausforderungen durch die Charakterisierung von Ni/GDC-Elektroden verschiedener Herstellungstechniken für den Betrieb bei mittleren Temperaturen sowie durch die Entwicklung von beschleunigten Test- und Vorhersagemethoden zur Abschätzung der langfristigen Degradation.

Zellen, die mittels Siebdruck mit Standard- und Feinpartikel-Pasten vom Forschungszentrum Jülich GmbH sowie durch Infiltration hergestellt wurden, wurden anhand ihrer initialen elektrochemischen Charakterisierung und strukturellen Analyse verglichen. Zellen aus Ni-Infiltration in GDC zeigten die beste Leistung, gefolgt von Feinpartikel-Paste, GDC-Infiltration in Ni und Standard-Paste. Die initiale Charakterisierung zeigt, dass die Leistung von Ni/GDC-Elektroden stark von Partikelgröße, Sintertemperatur und Reduktionsprotokoll abhängt, während Zwischenschichten und Leiterschichten einen geringeren Einfluss haben.

Um überlappende Verlustmechanismen zu dekonvolvieren, wurden symmetrische Zellen eingesetzt, die Schlüsselprozesse wie Gasdiffusion und Ladungstransfer isolieren. Sensitivitätsanalysen zeigten allgemeine Elektrodenprozesse über alle Zellen hinweg, mit geringfügigen Unterschieden bei der Gasdiffusion und einem unbekannten mittelfrequenten Signal. Ein Ersatzschaltbild (ECM) wurde etabliert, bestehend aus einem Transmission-Line-Modell für Elektrodenkinetik und drei RQ-Elementen für Gasdiffusion, mittelfrequente und hochfrequente Beiträge von Elektrolyt/Schnittstelle.

Für Langzeittests wurde ein neuartiger Multi-Zellen-Versuchsaufbau basierend auf dem *active-driven gas layer*-Konzept entwickelt, der simultane Impedanzmessungen mehrerer Zellen ermöglicht. Dieser Ansatz reduzierte experimentelle Kosten und Zeit erheblich, während die kontrollierten Gasumwandlungsbedingungen erhalten blieben. Parallele Multi-Zellen-Experimente zeigten pseudoinduktive Schleifen, wenn eine Zelle ihre Nachbarn deutlich übertraf. Dieses

Phänomen wurde auf unterschiedliche Gaskonsumierung oder -produktion benachbarter Elektroden zurückgeführt, was die Bedeutung der Zelluniformität in Multi-Zellen-Testmethoden unterstreicht.

Beschleunigte Alterungsprotokolle wurden auf Grundlage kurzfristiger Tests unter erhöhten Belastungen entwickelt. Tests bei erhöhten Temperaturen zeigten eine Abnahme des Polarisationswiderstands über 800 °C, möglicherweise im Zusammenhang mit der Ni-Oberflächendiffusion in die GDC-Zwischenschicht. Bei 900 °C beobachtetes GDC-Sintern deutete auf eine Elektroden-Reorganisation hin, die unter Betriebsbedingungen nicht dominant ist. Folglich wurden Zellen mit Zwischenschicht, schlechter Anfangsleistung oder unklarer Impedanz ausgeschlossen. Eine Siebdruckzelle des Typs V1.5a wurde für beschleunigte Lebensdauertests ausgewählt, mit Langzeit-EIS-Messungen zwischen 600 und 750 °C und 10–50 % Feuchtigkeit, wobei Referenzbedingungen periodisch aufgezeichnet wurden. Der Ladungstransferwiderstand wurde mittels CNLS-Analyse angepasst und zeigte thermisch und feuchteaktivierte Degradation. Ein Arrhenius (Potenzgesetz)-basierter Umrechnungsfaktor ermöglichte die Standardisierung aller Zeitreihendaten.

Die Degradation wurde als thermisch aktiviert identifiziert, wobei bei 750 °C unterschiedliche Mechanismen auftraten. Lebensdauer-Vorhersagemodelle, einschließlich Arrhenius, Potenzgesetzes, logarithmische Funktion und Äquivalenzzeit-Konzepts, zeigten bei einzelner Anwendung divergierende Ergebnisse. Eine verbesserte Konsistenz wurde durch die Kombination von Arrhenius-Degradation mit Potenz- oder Logarithmusfunktionen erzielt, weiter verfeinert durch die Einbeziehung des Äquivalenzzeit-Konzepts. Diese hybriden Ansätze zeigten robuste Vorhersagefähigkeit und ermöglichten die Extrapolation der Entwicklung des Ladungstransferwiderstands auf längere Zeiträume bei reduzierter Testdauer.

Diese Arbeit etabliert einen umfassenden Rahmen für das Verständnis und die prädiktive Modellierung der Ni/GDC-Anoden-Degradation und trägt zu potenziellen Strategien für effiziente SOFC-Tests, Lebensdauerverbesserung und beschleunigte Kommerzialisierung bei.

Abstract

SOFCs show promise for both stationary and mobile power applications. Efforts have focused on improving performance, durability, and cost. For stationary systems such as heat and power generators, a lifespan of 40,000–80,000 hours is expected (14), although conventional long-term testing is costly and impractical. This thesis addresses these challenges by characterizing Ni/GDC electrodes from different fabrication techniques targeting intermediate-temperature operation, and by developing accelerated testing and predictive modeling strategies to estimate long-term degradation.

For long-term testing, a novel multi-cell test method was developed based on the active-driven gas layer concept, enabling simultaneous impedance measurements of multiple cells. This approach significantly reduced experimental cost and time while maintaining controlled gas conversion conditions. Several experiments revealed pseudo-inductive loops when one cell significantly outperformed its neighbors. This phenomenon was attributed to mismatched gas consumption or production among neighboring electrodes, highlighting the importance of cell uniformity in this test method.

Cells fabricated by screen printing with usual and fine particle pastes from Forschungszentrum Jülich GmbH, as well as infiltration techniques, were compared in terms of initial electrochemical characterization and electrode structure. Cells from Ni infiltration into GDC exhibited the best performance, followed by fine particle paste, GDC infiltration into Ni, and usual paste. Initial characterization shows that Ni/GDC electrode performance strongly depends on particle size, sintering temperature, and reduction protocol, while the interlayer and conductive layer have a minor impact. To deconvolute overlapping loss mechanisms, symmetrical cells were employed, isolating key processes such as gas diffusion and charge transfer solely in the fuel electrode. Sensitivity analysis revealed general electrode processes in all cells, with minor differences in gas diffusion and an unidentified mid-frequency feature. An equivalent circuit model (ECM) was established, consisting of a transmission line model for electrode kinetics and three RQ elements for gas diffusion, intermediate-frequency (unidentified), and high-frequency electrolyte/interface contributions.

Accelerated stress test protocols were designed based on short-term tests at elevated stressors. Elevated temperature testing identified a decrease in polarization resistance above 800 °C, possibly

related to Ni surface diffusion into the GDC interlayer. GDC sintering observed at 900 °C indicated electrode reorganization that is not dominant under nominal operating conditions. Consequently, cells with an interlayer, poor initial performance, or ambiguous impedance behavior were excluded. A screen-printed cell type (V1.5a) was selected as the model cell for accelerated stress testing with continuous EIS measurements between 600–750 °C and 10–50% humidity, with reference conditions recorded periodically. Charge transfer resistance was fitted via CNLS analysis. An Arrhenius/ power law-based conversion factor enabled standardization of all time-series data.

Degradation was found to be thermally activated, with different mechanisms appearing/dominating above 725 °C. Lifetime prediction models, including Arrhenius, power-law, logarithmic, and equivalent time concept, exhibited divergent results when applied individually. Improved consistency was achieved by combining Arrhenius degradation with power-law or logarithmic functions, further refined by incorporating the equivalent time concept. These hybrid approaches demonstrated robust predictive capability, enabling extrapolation of charge-transfer resistance evolution to extended durations with reduced test time.

This work establishes a comprehensive framework for understanding and predictive modeling of Ni/GDC anode degradation, contributing to potential strategies for efficient SOFC testing, durability improvement, and accelerated commercialization.

Preface

The present dissertation is the result of my scientific work at the Institute of Applied Materials – Materials for Electrical Engineering (IAM-ET) at KIT. Many people contributed to the successful completion of this work, supporting, guiding, and inspiring me both personally and professionally, and I would like to express my heartfelt gratitude to them at this point.

First and foremost, I sincerely thank Prof. PD. André Weber for accepting me into the SOFC field despite my initial lack of experience. His continuous scientific guidance, trust, and encouragement have been instrumental for my personal and professional development and for the success of this work.

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The period from 2021 to 2024 at KIT has been both challenging and rewarding, providing invaluable experience in experimental research, collaborative projects, and scientific problem-solving. I am deeply grateful for the opportunity to learn, contribute, and grow as a researcher during this time.

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Acronyms and symbols

Acronyms

ALS	Adler-Lane-Steele Model
ASR	Area-Specific Resistance
AST	Accelerated Stress Test
AVG	Average
CPE	Constant Phase Element
CNLS	Complex Non-Linear Least Squares
DPB	Double-Phase Boundary
DRT	Distribution of Relaxation Times
ECM	Equivalent Circuit Model
EMF	Electromotive Force
ESC	Electrolyte-Supported Cell
FLW	Finite-Length Warburg Element
FIB/SEM	Focused Ion Beam / Scanning Electron Microscopy
GDC	Gadolinium-Doped Ceria
GFLW	Generalized Finite-Length Warburg Element
HF	High-Frequency
IAM – ET	Institute for Applied Materials – Electrochemical Technologies
KIT	Karlsruhe Institute of Technology
LEM	Laboratory for Electron Microscopy

LF	Low-Frequency
LSCF	Lanthanum Strontium Cobalt Ferrite
MF	Mid-Frequency
OCV	Open Circuit Voltage
PLD	Pulsed Laser Deposition
RQ	Resistance parallel to a Constant Phase Element
RC	Resistance parallel to a Capacitor
SOC	Solid Oxide Cell
SOFC	Solid Oxide Fuel Cell
STD	Standard Deviation
TLM	Transmission Line Model
TPB	Triple-Phase Boundary
YSZ	Yttria-Stabilized Zirconia (8YSZ)

Constants

k_B	Boltzmann constant, $1.380649 \cdot 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
$\hbar$	Reduced Planck constant, $1.054571817 \cdot 10^{-34} \text{ J s}$
R_g	Universal gas constant, $8.314 \text{ J}(\text{mol K})^{-1}$
F	Faraday constant, $96,485.3321 \text{ s A mol}^{-1}$
j	Imaginary unit
P_{cor}	Correction factor, $101,330 \text{ Pa atm}^{-1}$

Latin symbols and variables

a	Fitting parameter /-
A	Area / m^2

b	Fitting parameter / -
C	Capacitance / F
C_{ct}	Chemical capacitance / F
d	Thickness / m
d_i	Diameter of phase i / m
D	Diffusion coefficient / $\text{m}^2 \text{s}^{-1}$
$D_{\text{mol},i}$	Molar diffusion coefficient of gas component i / $\text{m}^2 \text{s}^{-1}$
$D_{\text{mol},ij}$	Molar diffusion coefficient of a material system consisting of gas components i and j / $\text{m}^2 \text{s}^{-1}$
E_{act}	Activation energy / J mol^{-1}
F_c	Conversion factor / -
f	Frequency / s^{-1}
G	Gibbs free energy / J mol^{-1}
G_0	Standard Gibbs free energy / J mol^{-1}
G_{EL}	Electrode geometry factor / -
i	Alternating current / A
i_0	Amplitude of alternating current / A
I	Amplitude of alternating current / A
j	Current density / Am^{-2}
j_0	Exchange current density / Am^{-2}
k	Degradation rate of charge transfer resistance/ $\Omega\text{cm}^3\text{s}^{-1}$
L	Length / m
$L_{\text{Diff,EL}}$	Characteristic diffusion length of electrode / m
n_i	Amount of substance i / mol
P	Power / W
p	Pressure / Pa

p_{H_2}	Hydrogen partial pressure / Pa
$p_{\text{H}_2\text{O}}$	Steam partial pressure / Pa
p_{O_2}	Oxygen partial pressure / Pa
R	Resistance / Ω
r_{ct}	Charge transfer resistance / Ωm^3
R_{ohm}	Ohmic resistance / Ω
R_{ct}	Differential charge transfer resistance / Ωm^{-1}
R_{eon}	Differential electronic resistance / Ωm^{-1}
R_{ion}	Differential ionic resistance / Ωm^{-1}
s	Stressor, can be temperature, humidity, and load / -
T	Temperature / K
t	Time / s
u	Alternating voltage / V
u_0	Amplitude of alternating voltage / V
U	Voltage / V
U_{cell}	Cell voltage / V
U_{Nernst}	Nernst voltage / V
U_{th}	Theoretical voltage / V
V	Volume / m^3
x_i	Mole fraction of gas component i / -
z	Number of electrons transferred / -
Z	Complex impedance / Ω
Z'	Real part of complex impedance / Ω
Z''	Imaginary part of complex impedance / Ω

Greek symbols and variables

Θ_D	Debye temperature / K
η	Overpotential / V
$\mu_e(T)$	Temperature-dependent electron mobility / $\text{m}^2 (\text{Vs})^{-1}$
$\mu_{\text{ion}}(T)$	Temperature-dependent ionic mobility / $\text{m}^2 (\text{Vs})^{-1}$
κ	The root of the ratio of the charge transfer resistance to the sum of the ionic and electronic path resistances / m
$\sigma_{\text{el}}(T)$	Temperature-dependent electronic conductivity / Sm^{-1}
$\sigma_{\text{ion}}(T)$	Temperature-dependent ionic conductivity / S m^{-1}
$\eta_{\text{Act,El}}$	Activation overpotential for electrode / V
$\eta_{\text{Act,An}}$	Activation overpotential for anode / V
$\eta_{\text{Act,Cath}}$	Activation overpotential for cathode / V
α_{EL}	Symmetry factor describing polarization of electrode / –
α_i	Thermal expansion coefficient / K^{-1}
δ	Concentration of oxygen vacancy / –
ψ	Microstructure parameter / –
ψ_{EL}	Microstructure parameter of the pores in an electrode / –
ω	Angular frequency / rad s^{-1}
ω_D	Debye characteristic frequency / s^{-1}
φ	Phase shift / rad
λ	Depth of electrochemical activity / Penetration depth / m
ε	Volume fraction / –
τ_i	Tortuosity of phase i / –
σ_{ij}	Lennard-Jones characteristic length of the system consisting of i and j / m
Ω_D	Collision integral / –

χ_i	Resistance of the i (electronic or ionic) rail in transmission line model / Ωm^{-1}
ζ	Impedance connecting the electronic and ionic rail in transmission line model / Ωm
Δ	Relative change / -

General deep indexes

a, age	Activation for aging
Act	Activation
An	Anode
bottom	Bottom
c	conversion
Cath	Cathode
cell	Cell
CPE, RQ	CPE in RQ configuration
ct	Charge transfer
ct, ref	Reference charge-transfer resistance
ct, $p_{\text{H}_2\text{O},i}$	Charge transfer at steam partial pressure $p_{\text{H}_2\text{O},i}$ of condition i
D	Debye
Diff, EL	Diffusion in electrode
eff	Effective
EL	Electrode
el	Electronic
eon, GDC	Electronic path in GDC
eon, Ni	Electronic path in Ni
GDC	GDC phase
Gerischer	Gerischer Element

g	Gas constant
H_2	Hydrogen
H_2O	Water / steam
HF	High-frequency
i	Cell or electrode index in assembly / Phase i / Gas species i
$i(j)$	In the electrode (j) of cell i
$i - j$	Between cell i and j
ij	In the space between cell i and j / The system consisting of components i and j
ideal	Ideal
ion	Ionic
ion, GDC	Ionic path in GDC
j	Component j
K_n	Knudsen diffusion
LF	Low-frequency
mea	Measurement
mea, sim	Simulation of measurement
MF	Middle-frequency
MIEC	Mixed ionic electronic conductor
mol	Molecular diffusion
n	Process index
Ni	Nickel
OCV	Open-circuit voltage
O_2	Oxygen
p	Pore
pore	Pore phase

Pol	Polarization
preset	Preset
sealed	Sealed space
th	Theoretical value
TLM	Transmission Line Model
top	Top
TPB	Triple-phase boundary
Warburg	Warburg element
YSZ	YSZ phase
δ	Defect-related factor / oxygen vacancies

1 Introduction

A reliable and sustainable energy supply is essential for modern society. However, rising global population and economic growth continue to drive energy demand, creating economic, ecological, and social challenges. In 2017, fossil fuels still accounted for 82% of the global energy supply (15). Even in Germany, where the energy transition is already progressing, fossil fuels take up 67% of total demand (15). The depletion of fossil resources and the acceleration of global warming indicate the urgent need for sustainable and efficient energy conversion technologies.

Fuel cells are regarded as a key technology in this transition. By directly converting chemical energy into electricity, fuel cells achieve electrical efficiencies of up to 60%, and when operated in combined heat and power mode, total efficiencies can approach 90% (16).

Despite their potential, large-scale commercialization of SOFCs is still hindered by challenges in (i) performance, (ii) lifetime, and (iii) cost reduction. Durability remains particularly critical, as degradation processes limit long-term reliability. While the widely used Ni/YSZ anode provides excellent performance, it suffers from poor tolerance to aging and sulfur poisoning.

In contrast, Ni/gadolinium-doped ceria (GDC) anodes have demonstrated significantly higher sulfur tolerance (17), attributed to the mixed ionic and electronic conductivity of GDC, which extends the electrochemically active area from the triple phase boundary to the entire electrode surface. Particularly at temperatures as low as 500 °C, the ionic conductivity of GDC is significantly higher than that of YSZ (18). This makes Ni/GDC a promising alternative and an intensively researched material.

At typical SOFC operating conditions, microstructural degradation processes evolve over long timescales, whereas practical lifetimes are expected to exceed ten years. To address this, accelerated stress testing (AST) has become an essential method, where degradation is accelerated through stressors and subsequently extrapolated to nominal conditions (19, 20, 21, 22). Such approaches are critical due to the limited availability of long-term data and the complex interplay of degradation mechanisms.

1.1 Motivation of this Work

To fully exploit the development potential of solid oxide fuel cells, it is crucial to understand the operating principles of all SOFC components and their aging behavior. Previous SOFC studies have shown that, in particular, the fuel electrode (anode) largely determines the performance, lifetime, and manufacturing costs at the single-cell level (23, 24, 25).

The development of high-performance Ni/GDC anodes for low-temperature operation ($\leq 600\text{ }^{\circ}\text{C}$) requires a deep understanding of the relationship between electrode microstructure and electrochemical behavior. Predicting long-term degradation remains challenging due to complex structural changes that differ from conventional Ni/YSZ electrodes (26, 27, 28). This complexity also complicates the design of AST protocols, which must selectively accelerate degradation mechanisms relevant under nominal operating conditions while excluding those dominant only at elevated stress levels.

The primary motivation of this work is to establish a systematic workflow for evaluating and predicting the degradation behavior of Ni/GDC electrodes under low-temperature operation, integrating electrode design optimization, multi-cell testing method development, AST protocol design, data analysis, and aging modeling:

1. Constructing a multi-cell testing setup to increase throughput, improve data reliability, and investigate the advantages and limitations of such an approach.
2. Characterizing electrodes with excellent performance at $600\text{ }^{\circ}\text{C}$ and establishing an equivalent circuit model.
3. Developing AST protocols that focus on relevant degradation mechanisms while avoiding artifacts from non-representative stressors.
4. Establishing robust data processing methods, including electrochemical impedance spectroscopy (EIS) analysis using the distribution of relaxation times (DRT) and complex nonlinear least squares (CNLS) fitting, to standardize the charge-transfer resistance and other key degradation parameters from the fitted data.
5. Developing semi-empirical aging models to predict long-term behavior under realistic operating conditions.

By combining multi-cell testing, electrode characterization, AST, data standardization processing, and modeling into a framework, this work aims to provide a reproducible methodology that can serve as a standard for the SOFC industry, supporting systematic electrode optimization and reliable lifetime assessment.

1.2 Outline

The following chapters of this thesis present the theory, methodology, results, and analysis undertaken to achieve the objectives of this work:

- **Chapter 1** provides a brief introduction to SOFCs, their applications, and the challenges associated with commercialization. It summarizes the goal and motivation of the thesis.
- **Chapter 2** presents the theoretical background of SOFCs, including their materials groups, working principle, and loss mechanisms. This is followed by a literature review on degradation phenomena as a function of operating conditions, and an overview of concepts such as AST, along with common degradation models, EIS, common equivalent circuit models (ECM), and data analysis using DRT and CNLS.
- **Chapter 3** provides a detailed overview of the topography of the tested cells, their fabrication techniques, and corresponding microstructural characterization techniques. It also describes the experimental setup, including the gas-driven layer concept and methods implemented.
- **Chapter 4** presents the experimental results. The first part describes a physical electrochemical model to simulate the pseudo-inductive loop observed in impedance measurements. The second part compares area-specific resistance (ASR) for different fabrication procedures. The third part presents the identification of the electrode processes and the establishment of the ECM. The fourth part describes pre-tests for designing AST protocols. The fifth part illustrates the results of durability tests on the selected model cell type and the novel data processing method. The last part presents several semi-empirical aging models with robust predictive capability.
- **Chapter 5** summarizes the findings of this study, provides conclusions, and discusses perspectives for future research.

2 Fundamentals

In the first part of this chapter, the working principle of an SOFC is described. Common materials applied to each component of the cell are briefly introduced.

The third part of the chapter provides a brief introduction to the loss mechanisms in SOFCs.

The fourth part of this chapter introduces methods to enhance electrode performance for low-temperature operation.

The following section lists the various aging mechanisms in SOFCs, with a focus on anode degradation. The similarities and differences between Ni/YSZ and Ni/GDC anodes are briefly discussed.

The next part introduces and discusses the necessity for applying accelerated stress testing for lifetime prediction. Commonly used degradation models for SOFCs are noted.

The seventh section of the chapter provides a brief introduction to electrochemical impedance spectroscopy. Subsequently, common impedance elements used to model the impedance response of the SOFC single cell in previous works are presented.

Finally, the complex nonlinear least-squares fitting procedure and the distribution-of-relaxation-times approach are discussed.

2.1 Working Principle of Solid Oxide Fuel Cells

The underlying functional principle of the fuel cell was first discovered in 1838 by Christian Friedrich Schönbein and was reported by Sir William Robert Grove in 1839 as a new technology, and was named the galvanic gas battery (29). Like a battery, the fuel cell provides a voltage that can be used to perform electrical work. The energy is chemically stored in the fuel gas and released through a redox reaction between the fuel gas and the oxidant. The energy released is accessible as electrical energy from the redox reaction occurring in spatially separated porous electrodes. The solid oxide fuel cell (SOFC) is a special type of fuel cell that, due to its high operating temperatures above 500 °C, can convert not only hydrogen but also conventional fuels

such as natural gas into electrical energy. The electrodes are separated by a gas-tight electrolyte conducting only oxygen ions. Typically, hydrogen is used as the fuel gas at the anode and oxygen as the oxidant at the cathode, so that the product according to equation (2.1) is gaseous water. The driving force of the fuel cell is the chemical potential difference of the oxygen partial pressure between the cathode and the anode. Accordingly, the reaction is at equilibrium on the product side, water. During operation, the gases are continuously supplied, enabling long-term operation lasting thousands of hours.

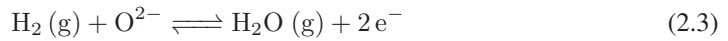
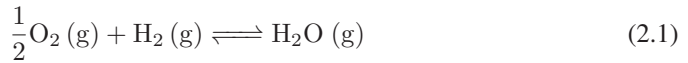


Figure 2.1 shows a simplified functional principle of a SOFC. The reduction of oxygen occurs according to (2.2) within the cathode on the surface of the electronic and ionic conductive material. Gaseous oxygen is reduced to an oxygen ion by absorbing two electrons and diffuses into the cathode solid.

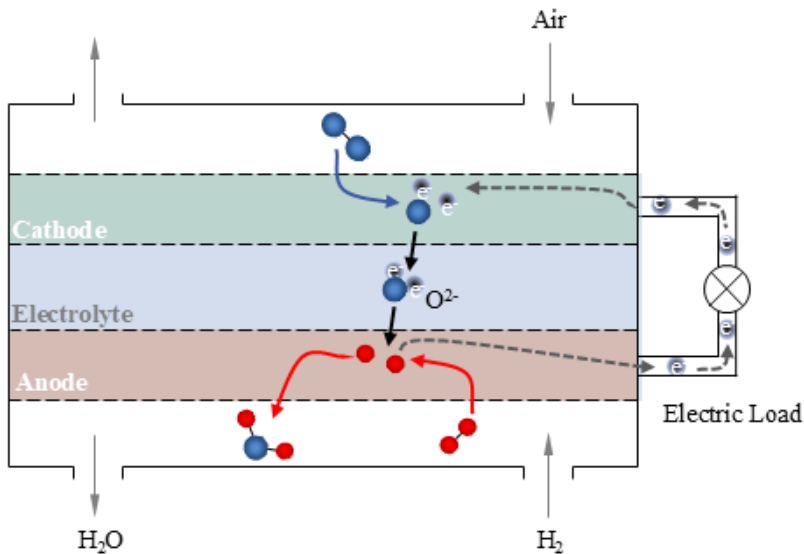


Figure 2.1: The functional principle of a solid oxide fuel cell operating with hydrogen as fuel and oxygen as oxidant. The blue balls indicate oxygen atoms, the gray balls for electrons, and the red balls for hydrogen atoms.

The ions then cross the cathode/electrolyte interface and diffuse further through the electrolyte to the anode. According to equation (2.3), electro-oxidation with hydrogen (H_2) to water (H_2O) takes place here.

The electrons released are transported via an electronically conductive phase within the anode. When the reaction is in equilibrium, an electrical potential difference is established between the electrodes. The electrons then flow back to the cathode via the external circuit.

In the unloaded case (open-circuit voltage, OCV), the transport of O^{2-} ions through the electrolyte results in a potential difference between the electrodes. As the potential difference increases, the diffusion current vanishes, and an equilibrium state is reached. The resulting cell voltage U_{th} at equilibrium can generally be calculated from the free reaction enthalpy $\Delta_R G$ of the overall reaction:

$$U_{th} = -\frac{\Delta_R G}{z \cdot F} \quad (2.4)$$

where z represents the number of charge carriers involved in the reaction (here: O^{2-} for $z = 2$), and F denotes the Faraday constant.

The influence of the oxygen gradient between anode and cathode on the cell voltage can be expressed by the Nernst equation (30). The concentration dependent voltage, also called Nernst voltage U_{Nernst} , can be calculated from the universal gas constant R_g , the absolute temperature T , and the oxygen partial pressures $p_{O_2, Cat}$ and $p_{O_2, An}$ of the supplied gases at the cathode and anode:

$$U_{Nernst} = U_{th} = \frac{R_g \cdot T}{2 \cdot F} \ln \sqrt{\frac{p_{O_2, Cat}}{p_{O_2, An}}} \quad (2.5)$$

Considering the law of mass action, Equation (2.5) can be rearranged (31):

$$U_{Nernst} = -\frac{\Delta_R G^0}{2 \cdot F} + \frac{R_g \cdot T}{2 \cdot F} \ln \frac{\sqrt{p_{O_2, Cat}} \cdot p_{H_2, An}}{p_{H_2O, An}} \quad (2.6)$$

Here, $\Delta_R G^0$ represents the free reaction enthalpy under standard conditions ($T = 298.15$ K and $p = 1$ bar). Thus, the cell voltage can be calculated depending on the actual composition of the supplied gases.

In the loaded case, the cell voltage falls below the thermodynamically predicted Nernst voltage because all reaction and transport processes in the cell are associated with losses. The *ASR*

serves as a measure of the cell's internal losses. The reduced cell voltage can be calculated from the product of the applied current density j and the total cell resistance ASR_{Cell} :

$$U_{\text{cell}} = U_{\text{Nernst}} - j \cdot ASR_{\text{Cell}} = U_{\text{Nernst}} - j \sum_n ASR_n \quad (2.7)$$

The cell resistance ASR_{Cell} can be measured using impedance spectroscopy (Section 2.7). By evaluating the measurement data with suitable methods (Section 2.9) and appropriate modeling approaches (Chapter 2.8), all loss contributions ASR_n can be quantified and assigned to their physical origin. The processes related to these loss contributions are introduced in Section 2.3.

2.2 Cell Materials

The SOFC is a ceramic composite structure consisting of three components: cathode, electrolyte, and anode (Figure 2.1). For the functionality and reliability of the cell, it is important that (i) the electrode reactions (Equations (2.2) and (2.3)), (ii) the charge transport (O_2^- and e^-), and (iii) the supply of reactants (H_2 and O_2) to the reaction zone, as well as the removal of products (H_2O), must occur quickly and efficiently. Sustained operation is only ensured if each cell component demonstrates: (i) stability at high temperatures, (ii) stability in reducing and/or oxidizing atmospheres, (iii) chemical compatibility with adjacent components, and (iv) comparable thermal expansion coefficients.

The following sections introduce common materials used for the production of SOFC single cells. In keeping with the focus of this work, particular attention is given to anode materials, which are discussed in Section 2.2.2.

2.2.1 Electrolyte and Cathode Materials

Electrolyte Materials

Most electrolytes are ceramic materials, capable of conducting ions and providing a gas-tight separation between the anode and the cathode. Both proton- and oxygen-ion-conducting materials are suitable. Generally, they should meet the following requirements (32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43):

- Low cost and easy fabrication.

- Chemical, phase, thermal, dimensional, and morphological stability.
- Sufficient mechanical strength against thermal stress.
- Low electronic conductivity.
- High oxide ion or proton conductivity to minimize ohmic losses.

Yttria-stabilized zirconia is commonly used as an electrolyte in fuel cells. Scandia-stabilized zirconia exhibits higher conductivity than YSZ at lower temperatures due to the smaller difference in ionic radii between Sc^{3+} and Zr^{4+} , which leads to fewer defects, higher mobility, and a more compact crystal structure. However, this advantage vanishes below 500 °C due to increased activation energy. Additionally, a higher Scandia content (typically >8%) transforms the cubic structure into a rhombohedral structure, reducing conductivity at lower operating temperatures. Grain boundaries are another crucial factor in intermediate-temperature SOFCs (IT-SOFCs), as their contribution to resistance increases at reduced temperatures (44). Nanostructured materials have been developed to improve grain-boundary properties and are widely used in IT-SOFC electrolytes.

Gadolinium-doped ceria is another promising electrolyte material, exhibiting higher conductivity at low temperatures compared to YSZ or ScSZ (43). However, challenges such as mechanical stability, mixed ionic/electronic conduction at low oxygen partial pressures, cost, and the limited availability of gadolinium prohibited widespread use.

While extensive research has focused on alternative electrolyte categories, such as ScSZ for low-temperature applications (44), various doped perovskite systems like LSGM (45, 46), or vast ranges of proton-conducting oxides (47, 48), these materials often face severe trade-offs regarding mechanical stability, electronic leakage, complex synthesis pathways, or high material costs. Comprehensive overviews of these broad, alternative electrolyte categories are detailed in several reviews (49, 50, 51, 52). Among state-of-the-art oxygen-ion conductors, YSZ remains the standard material with extraordinary chemical and mechanical stability across a wide temperature range, making it highly reliable for electrochemical studies.

Cathode Materials

Perovskite-structured compounds, always denoted as ABO_3 , exhibit distinctive properties due to the integration of A- and B-cations within their structure. Typically, alkali metals, rare-earth metals, alkaline earth metals, elements from the 6th period, and group 13–15 cations occupy the A-site, forming a cubic close-packed structure. This arrangement is facilitated by the comparable size of O^{2-} ions and the presence of octahedral voids occupied by B-cations. The electronic

properties of perovskite materials can be tuned by the degree of distortion and partial substitution in both A- and B-cation sublattices. Interactions between the oxygen $2p$ -orbitals and the d -orbitals of transition metals lead to the formation of wide energy bands. Lattice distortions narrow these bands, leading to dielectric effects and the localization of electronic states due to octahedral rotation. The conductivity of perovskites is strongly dependent on structural distortion. For instance, doping perovskites with rare-earth ions increases distortion due to their smaller ionic radii. The selection of perovskite-type cathode materials depends on the oxidation state variations of transition metal oxides. Higher oxidation states, such as $4d$ and $5d$ elements, typically exhibit higher conductivity, while $3d$ elements may be unstable under oxidative cathode atmospheres. Perovskite-type transition metal oxides, such as LaMO_3 ($M = \text{Mn, Cr, Co, Ni, Fe}$), demonstrate p-type conductivity and stability within specific temperature ranges under oxidizing conditions (53).

The thermal expansion coefficient (TEC) is a critical parameter for perovskite cathodes in SOFCs, as it must be compatible with other fuel cell components. It is influenced by electronic, ferroelectric, and magnetic properties, as well as chemical composition. Increasing temperature generally enhances oxygen vacancies and metal–oxygen bond strength. Cobalt-containing perovskites show high TEC and reactivity with YSZ electrolytes. Protective layers of GDC can mitigate this reactivity, although adding to diffusion complexities during long-term SOFC operation. Partial substitution of cobalt with other B-site cations (Mn, Ni, Fe, Cu) can help control this drawback (54). For example, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ composites demonstrate high conductivity, catalytic activity, and oxygen self-diffusion at SOFC operating temperatures (53).

The state of the art, fundamental mechanisms, and degradation phenomena of the cathode materials are summarized in several reviews (55, 50, 51, 56, 57, 58).

2.2.2 Anode Materials

The selection of anode materials is a critical aspect of SOFC technology, as it is decisive for electrochemical performance, microstructure, and cell fabrication. An ideal anode should possess several key properties to ensure optimal performance. First, it should provide a large surface area at the TPB, where the electrochemical reaction occurs among the electronic conductor, oxygen-ion conductor, and fuel gas. Second, the anode must have a porous microstructure to enable rapid gas transport and removal of reaction products. Additionally, anode materials must demonstrate stability, high electronic conductivity, compatibility with other cell components at elevated temperatures, and high electrocatalytic activity. Although noble metals can extend TPB in electrodes and accelerate charge transfer, their high cost and limited availability often make them impractical for large-scale applications.

Nickel is the most commonly used anode material, typically in a composite with an electrolyte such as YSZ (59). This ceramic-metal composite, also known as a Cermet, contains both an electronically conductive phase and an ionic conductive phase, interpenetrating each other. The structure increases TPB length and compensates for the high TEC of nickel, $\alpha_{\text{Ni}} = 18 \cdot 10^{-6} \text{ K}^{-1}$ (60). For a Ni/8YSZ cermet with 40 vol.% nickel, the TEC is $\alpha_{\text{Ni}/8\text{YSZ}} = 12.5 \cdot 10^{-6} \text{ K}^{-1}$ (61). At SOFC operating conditions, nickel exists as metallic Ni in a reducing fuel atmosphere and as NiO in air. Partial or complete re-oxidation of Ni can lead to volume expansion up to 30%, resulting in mechanical stresses, microstructural degradation, or even electrolyte cracking (62).

Moura's review (63) highlighted porous metals (Fe, Ag, Pt, Co, Ni, Ru, Mn) as candidate electrodes for LT-SOFCs, emphasizing Ni due to its low melting point and sintering temperature. However, limitations remain, such as poor adhesion to dense electrolytes and mismatched thermal expansion coefficients regarding GDC and YSZ.

Re-oxidation may be caused by seal leaks, fuel supply failure, system shutdown, or high temperature and water vapor partial pressures, which can induce Ni particle agglomeration. Agglomeration reduces the volume-specific TPB length, increasing anode polarization losses (64, 65, 66, 67, 68). Consequently, alternative redox-stable anodes based on MIEC ceramics are being considered. These materials show higher tolerance to impurities such as H_2S (59, 69). Cowin et al. (70) highlighted that composite anodes require high electrocatalytic activity, thermal and chemical stability, high ionic/electronic conductivity, and redox cycling tolerance with compatible TECs.

Electrochemical properties of ceria/zirconia-based ceramics such as $\text{Ce}_{0.6}\text{Gd}_{0.4}\text{O}_{2\pm\delta}$ and $\text{Y}_{0.2}\text{Ti}_{0.18}\text{Zr}_{0.62}\text{O}_1$ (Yzt) have been studied. The polarization resistance of sintered Yzt electrodes was $0.7 \text{ } \Omega\text{cm}^2$ at $1300 \text{ } ^\circ\text{C}$. In contrast, the polarization resistance without sintering for the two ceramic electrodes was found to be 0.44 and $3.7 \text{ } \Omega\text{cm}^2$, respectively. Liu et al. (71) developed Ni-exsolved $\text{Ba}(\text{Ce}_{0.9}\text{Y}_{0.1})_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ /GDC composite anodes showing long term stability in CH_4 fuel.

Recent studies have shifted attention to Ni/GDC nanocomposites as effective alternatives to Ni/YSZ. Chavan et al. (72) investigated Ni/GDC nanocomposites and found that higher NiO content decreased activation energy, suggesting enhanced performance, while lower NiO content provided a better-connected GDC grain network. Gil et al. (73) synthesized Ni/GDC powder with a 50:50 wt% ratio via a polymer-based complex solution, producing an interconnected porous microstructure that enhanced the TPB. Chen et al. (74) deposited Ni/GDC films on GDC substrates using electrostatic-assisted ultrasonic spray pyrolysis. At $450 \text{ } ^\circ\text{C}$, with a 50:50 composition and an applied voltage of 12 kV, they observed a high density of TPBs. Ding et al. (75) further advanced this work by fabricating single cells with LSCF nanoparticles printed over Ni/GDC|GDC, prepared via hydroxide co-precipitation.

2.3 Loss Mechanisms

The functionality and performance of an SOFC are directly related to the internal reaction and transport processes. For a complete physicochemical description, all internal mechanisms must be considered in every component. In this work, the chosen cell type is the symmetrical Ni/GDC electrolyte-supported cell (ESC) manufactured by Forschungszentrum Jülich GmbH (cell details in Section 3.1). Accordingly, the following sections focus on the anode, with brief introductions to electrolyte and cathode processes. Operation with H_2 as fuel is considered, and a detailed discussion of electrochemical loss processes is provided.

2.3.1 Charge Transport

During the transport of charge carriers (electrons and ions) within an electrochemical system, ohmic losses arise due to the finite conductivity of each component. The overall ohmic resistance is the sum of individual contributions R_n (n denotes each cell component). Ohm's law summarizes the linear relationship between the current density j and the ohmic overpotential η_{ohm} :

$$\eta_{\text{ohm}} = j \cdot R_{\text{ohm}} \quad (2.8)$$

Based on the geometry and the material-specific conductivity, the ohmic resistance can be calculated as:

$$R_{\text{ohm}} = \frac{L}{\sigma_{\text{el/ion}}(T) \cdot A} \quad (2.9)$$

where L is the length of the conductor, A the cross sectional area, and $\sigma_{\text{el/ion}}(T)$ the temperature-dependent electronic or ionic conductivity. In planar ESCs, the main contribution to ohmic losses comes from the transport of oxygen ions in the solid electrolyte for its thickness. For the investigated cells, 8YSZ remains the state-of-the-art electrolyte material. Detailed descriptions of charge transport in mixed-conducting LSCF cathodes can be found in (65).

Depending on electrode composition and microstructure, charge transport in the electrodes can lead to additional ohmic losses. In the fuel electrode, both electronic transport through the metallic phase (Ni) and oxygen ionic transport through the ceramic phase (10GDC) must be considered. A more detailed description of charge transport in mixed-conducting electrodes is provided in (59).

Metallic Conductor

In metallic conductors, intrinsic conductivity is defined by the charge carrier density n_e , the elementary charge e , and the electron mobility μ_e :

$$\sigma_{\text{el}}(T) = n_e \cdot e \cdot \mu_e(T) \quad (2.10)$$

The Drude model (60) describes electron conduction in metals, where the lattice is considered as positively charged atomic cores with free electrons moving stochastically. This free electron movement results in high thermal and electrical conductivity. When an external electric field is applied, electrons are accelerated through the lattice until scattering occurs. The mean collision time decreases with increasing temperature, reducing electron mobility μ_e and thus conductivity.

The quantum-mechanical Sommerfeld model extends the Drude model by considering the thermal motion of lattice atoms as phonons. The Bloch-Grüneisen law describes the interaction between phonons and electrons, influencing metallic resistivity (61, 62):

$$\rho_{\text{el}}(T) = \frac{1}{\sigma_{\text{el}}(T)} = \frac{4\pi}{3} \cdot \frac{k_F^2 \cdot E_F \cdot \Omega_0}{e^2 \cdot k_B \cdot \Theta_D \cdot v_F^2 \cdot M} \cdot \left(\frac{T}{\Theta_D} \right)^5 \cdot \int_0^{\Theta_D/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} \quad (2.11)$$

Key parameters include the Fermi surface radius k_F , Fermi energy E_F , electron velocity v_F , unit cell volume Ω_0 , atomic mass M , and Debye temperature Θ_D , calculated with the Debye frequency ω_D as (64):

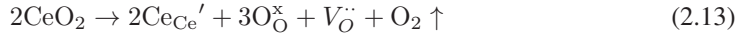
$$\Theta_D = \frac{\hbar \omega_D}{k_B} \quad (2.12)$$

At low temperatures ($T < \Theta_D$), conductivity follows a T^5 dependence ($\sigma \propto T^{-5}$), while at high temperatures ($T > \Theta_D$), a linear dependence occurs ($\sigma \propto T^{-1}$). Nickel, with a Debye temperature of 450 K ($\sim 177^\circ\text{C}$), is commonly used in anodes and operates within the linear range for relevant temperatures.

Ceramic Conductor

Functional transition metal and rare-earth oxide ceramics can exhibit metallic, semiconducting, or insulating properties depending on their defect chemistry and the surrounding atmosphere.

GDC represents a classic example of this environmental dependency. In intermediate oxidizing environments, GDC acts predominantly as an ionic conductor with negligible electronic leakage (Figure 2.2(b)). However, when exposed to reducing fuel atmospheres, a portion of the Ce^{4+} cations undergoes a reduction to Ce^{3+} , leading to the formation of oxygen vacancies and releasing small polaron electronic carriers into the lattice (Equation 2.13).



Consequently, under operating conditions, GDC exhibits characteristic semiconducting behavior (76, 77). According to the defect equilibrium analysis by Smyth (67), the dependence on the oxygen partial pressure is consistent with n -type conductivity at low p_{O_2} , as shown in Figure 2.2.

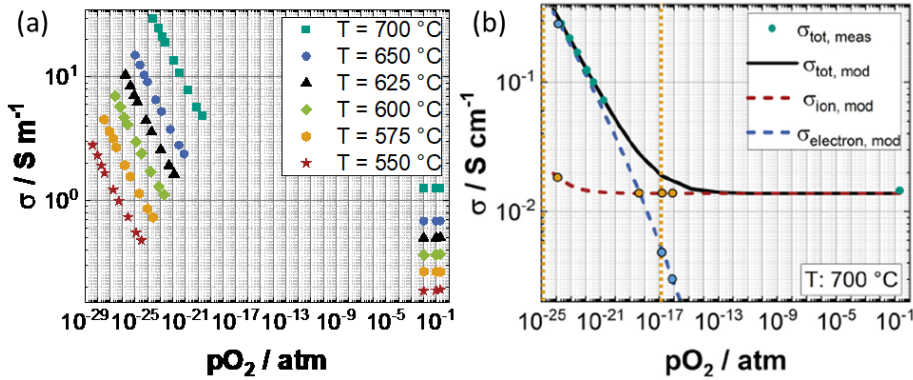


Figure 2.2: (a) Total bulk conductivity of GDC measured at different temperatures and atmospheres. Adapted from (78). (b) Measured conductivity (green), modeled bulk conductivity (black), calculated ionic (red) and electronic (blue) conductivity over p_{O_2} . Adapted from (79).

Ceria forms a chemically stable cubic fluorite structure (Fm-3m) with no reported phase changes up to its melting point of ~ 2750 K (66). Undoped ceria exhibits relatively low electrical conductivity at atmospheric oxygen partial pressures. Doping with Gd^{3+} enhances the conductivity through the defect reaction in equation 2.14, which leads to the formation of oxygen vacancies.

In this system, oxygen vacancies and small polarons enable ionic and electronic hopping mechanisms (68). Analogous to the electronic conductivity in metals, both ionic and electronic conductivity can be expressed as the product of the number of free charge carriers and their mobility μ_i (77):

$$\sigma_{\text{eon}} = \mu_{\text{eon}} e [\text{Ce}'_{\text{Ce}}], \quad \sigma_{\text{ion}} = \mu_{\text{ion}} 2e [V_{\text{O}}^{\bullet\bullet}] \quad (2.15)$$

Mobility is related to the self-diffusion coefficient $D_i(T)$ described by the Nernst-Einstein relation:

$$\mu_i(T) = \frac{q_i D_i(T)}{k_B T} \quad (2.16)$$

where i denotes the electronic or ionic charge carrier. The hopping process is temperature activated with activation energy E_{act} , following an Arrhenius law:

$$D_i(T) = D_{i,0} \exp\left(-\frac{E_{\text{act}}}{k_B T}\right) \quad (2.17)$$

where $D_{i,0}$ denotes a material-specific constant related to the lattice properties of doped CeO_2 . Combining these expressions results in the temperature-dependent conductivity, as shown in Figure 2.2(a).

Under oxidizing conditions, the concentration of oxygen vacancies is primarily determined by the amount of Gd dopant and therefore remains nearly constant. As a result, the ionic conductivity is dominated by the dopant-induced oxygen vacancies and exhibits only a weak dependence on oxygen partial pressure, as shown in Figure 2.2(b).

In contrast, the electronic conductivity is strongly affected by changes in oxygen partial pressure. Under reducing conditions, partial reduction of Ce^{4+} to Ce^{3+} generates electrons, leading to an increase in electronic conductivity. Therefore, decreasing oxygen partial pressure results in a larger electronic contribution to the total conductivity.

Consequently, GDC behaves predominantly as an oxygen-ion conductor under oxidizing conditions, whereas under reducing atmospheres it exhibits mixed ionic–electronic conduction due to the increasing concentration of electronic charge carriers.

In porous electrodes, the effective conductivity is reduced by a microstructural factor ψ :

$$\sigma_{\text{eff},i} = \psi_i \cdot \sigma_i \quad (2.18)$$

This reduction in conductivity can be attributed to two main factors. First, the porous matrix has a smaller effective volume for charge transport. Second, the charge carriers experience longer transport paths within the porous structure, described by the tortuosity (τ). The microstructural factor ψ is therefore defined as the ratio of the volume fraction ε_i of material i to its tortuosity τ_i :

$$\psi_i = \frac{\varepsilon_i}{\tau_i} \quad (2.19)$$

2.3.2 Mass Transport

In general, mass transport in SOCs is dominated by two primary mechanisms: diffusion and convection. The supply of operating gases through gas channels occurs primarily via convective flow driven by a pressure gradient. However, within the porous electrodes, convective flow is negligible, and reactant and product transport is dominated by gas diffusion driven by concentration gradients. Depending on the electrode structure, both molecular diffusion, in which molecular collisions dominate, and Knudsen diffusion, in which gas-wall collisions prohibit transport, must be considered.

In Joos' study (69), the microstructure of an SOC with an LSCF air electrode and Ni/YSZ fuel electrode was investigated, revealing a pore diameter d_p in the range of 400-600 nm. If the mean free path is comparable to or larger than the pore diameter d_p , Knudsen diffusion must be considered, as previously decided for Ni/YSZ fuel electrodes (65, 80, 81, 82). The pore diameter of the Ni/GDC fuel electrode used in this study is of a similar magnitude to the Ni/YSZ electrode (54), indicating that Knudsen diffusion should also be considered.

2.3.2.1 Calculation of Diffusion Coefficients

For any gas component i , the effective diffusion coefficient $D_{\text{eff},i}$ is given by:

$$D_{\text{eff},i} = \psi_{\text{EL}} \cdot D_i \quad (2.20)$$

where ψ_{EL} accounts for the porous microstructure of the electrode, where the pores deviate from an ideal cylindrical geometry (83).

If Knudsen diffusion is considered, the diffusion coefficient D_i is determined using the Bosanquet relation (84):

$$\frac{1}{D_i} = \frac{1}{D_{\text{mol},i}} + \frac{1}{D_{\text{Kn},i}} \quad (2.21)$$

Here, $D_{\text{mol},i}$ is the molecular diffusion coefficient, and $D_{\text{Kn},i}$ is the Knudsen diffusion coefficient.

For a binary gas mixture, the molecular diffusion coefficient $D_{\text{mol},ij}$ is calculated using the Chapman-Enskog equation (85):

$$D_{\text{mol},ij} = 1.86 \cdot 10^{-3} \frac{T^{1.5} \left(\tilde{M}_i^{-1} + \tilde{M}_j^{-1} \right)^{0.5}}{p \sigma_{ij}^2 \Omega_D} \quad (2.22)$$

The binary molecular diffusion coefficient $D_{\text{mol},ij}$ in Equation 2.22 describes the diffusion of component i in the presence of component j . It depends on the temperature ($T^{1.5}$) and is inversely proportional to the total pressure p . In this study, p is fixed at 1 atm for all measurements, allowing us to neglect this factor. For pure molecular diffusion in a binary mixture, component i diffuses in j at the same rate as j in i , such that $D_{\text{mol},ij} = D_{\text{mol},ji}$. The calculation is also based on the molar masses of the individual components $\tilde{M}_i$ and $\tilde{M}_j$, the collision integral Ω_D , and the Lennard-Jones characteristic length σ_{ij} . A detailed description of the determination of Ω_D and σ_{ij} can be found in (86).

For gas mixtures with more than two components, the Wilke approach is used (87):

$$D_{\text{mol},i} = \frac{1 - \tilde{y}_i}{\sum_{j \neq i} \tilde{y}_j (D_{\text{mol},ij})^{-1}} \quad (2.23)$$

where $\tilde{y}_i$ and $\tilde{y}_j$ are the mole fractions of the respective components.

The Knudsen diffusion coefficient is expressed as:

$$D_{\text{Kn},i} = \frac{d_p}{3} \sqrt{\frac{8R_g T}{\pi \tilde{M}_i}} \quad (2.24)$$

This coefficient is proportional to the pore diameter d_p , inversely proportional to the square root of the molar mass $\tilde{M}_i$, and has a temperature dependency of $T^{0.5}$ (85).

The resulting mass-transport resistances at the fuel electrode (82) and the air electrode (88), which depend on these diffusion coefficients, can be derived for performance modeling.

2.3.2.2 Mass Transport in Fuel Electrode

The diffusion overpotential $\eta_{\text{Diff,EL}}$ can be derived from the Nernst equation 2.5:

$$\eta_{\text{Diff,EL}} = \frac{R_g T}{2F} \ln \left[\frac{(p_{\text{H}_2\text{O,EL}})^{\text{TPB}} \cdot p_{\text{H}_2,\text{EL}}}{p_{\text{H}_2\text{O,EL}} \cdot (p_{\text{H}_2,\text{EL}})^{\text{TPB}}} \right] \quad (2.25)$$

In this equation, the partial pressures of hydrogen $(p_{\text{H}_2,\text{BE}})^{\text{TPB}}$ and water vapor $(p_{\text{H}_2\text{O,BE}})^{\text{TPB}}$ at the TPB are unknown. These two terms are derived from the work of Primdahl (82), as illustrated below.

Before the derivation, it is assumed that (i) stationary mass transport and (ii) the stagnant gas layer are present. Besides, (iii) the concentration gradients within this layer show a fully (iv) linear character. Furthermore, (v) no concentration gradients occur in the core volume. (vi) Convective entrainment flows are neglected.

A net flow can be neglected, since those of hydrogen and water vapor cancel each other out due to opposite flow directions, according to the Dusty Gas Model (DGM) (89). It is also assumed that the total gas pressure in the porous electrode remains constant (90). The diffusion coefficient is assumed to be independent of the concentration of the species. The mass flow density $\dot{n}_i$ of component i can therefore be described based on Fick's law in equation 2.26, taking into account the effective diffusion coefficient $D_{\text{eff},i}$:

$$\dot{n}_i = -D_{\text{eff},i} \frac{\partial \tilde{c}_i}{\partial s} \quad (2.26)$$

Here, $\tilde{c}_i$ represents the molar concentration of component i and s the diffusion path.

According to Faraday's law, the magnitude of the mass flow densities of hydrogen $\dot{n}_{\text{H}_2}$, and water vapor $\dot{n}_{\text{H}_2\text{O}}$ are proportional to the applied electric current density j :

$$|\dot{n}_{\text{H}_2}| = |\dot{n}_{\text{H}_2\text{O}}| = \frac{j}{2F} \quad (2.27)$$

Assuming ideal gas behavior, the molar concentration of the gas $\tilde{c}_i$ can be calculated from the ideal gas law as a function of the partial pressure p_i (in atm), the temperature T , and the universal gas constant R_g :

$$\tilde{c}_i = \frac{N_i}{V} = \frac{p_i}{R_g T} \cdot P_{\text{cor}}$$

where P_{cor} represents a correction factor of $101,330 \text{ Pa atm}^{-1}$.

By setting Equations 2.26 and 2.27 equal to each other and then integrating over the characteristic diffusion length $L_{\text{Diff,EL}}$ of the fuel electrode, an expression for the change of partial pressure Δp_i between the fuel gas flow and the electrode surface can be obtained. The partial pressure of hydrogen and water vapor at the reaction zone is:

$$(p_{\text{H}_2, \text{EL}})^{\text{TPB}} = p_{\text{H}_2, \text{EL}} - \frac{R_g T L_{\text{Diff, EL}}}{2F D_{\text{eff, H}_2} P_{\text{cor}}} \cdot j \quad (2.28)$$

$$(p_{\text{H}_2\text{O}, \text{EL}})^{\text{TPB}} = p_{\text{H}_2\text{O}, \text{EL}} + \frac{R_g T L_{\text{Diff, EL}}}{2F D_{\text{eff, H}_2\text{O}} P_{\text{cor}}} \cdot j \quad (2.29)$$

The diffusion overpotential at the fuel electrode can now be expressed as a function of the partial pressures of hydrogen $(p_{\text{H}_2, \text{EL}})^{\text{TPB}}$ and water vapor $(p_{\text{H}_2\text{O}, \text{EL}})^{\text{TPB}}$ at the triple-phase boundary by integrating Equations 2.28 and 2.29 into 2.25:

$$\eta_{\text{Diff, EL}} = \frac{R_g T}{2F} \ln \left[\frac{1 + \frac{R_g T L_{\text{Diff, EL}}}{2F D_{\text{eff, H}_2\text{O}} p_{\text{H}_2\text{O}, \text{EL}} \cdot P_{\text{cor}}} \cdot j}{1 - \frac{R_g T L_{\text{Diff, EL}}}{2F D_{\text{eff, H}_2} p_{\text{H}_2, \text{EL}} \cdot P_{\text{cor}}} \cdot j} \right] \quad (2.30)$$

Applying the logarithmic quotient rule and then Ohm's law, the derivative $\left. \frac{\partial \eta_{\text{Diff, EL}}}{\partial j} \right|_{j=0}$ under OCV results in the diffusion transport resistance $R_{\text{Diff, EL}}$ at the fuel electrode, as shown below (82):

$$R_{\text{Diff, EL}} = \left(\frac{R_g T}{2F} \right)^2 \cdot L_{\text{Diff, EL}} \cdot \left(\frac{1}{D_{\text{eff, H}_2} \cdot p_{\text{H}_2, \text{EL}}} + \frac{1}{D_{\text{eff, H}_2\text{O}} \cdot p_{\text{H}_2\text{O}, \text{EL}}} \right) \cdot \frac{1}{P_{\text{cor}}} \quad (2.31)$$

2.3.3 Charge Transfer

At the electrode/electrolyte interfaces, oxygen ions are incorporated into or extracted from the electrolyte via electrochemical reactions. Depending on the electrode type, these reactions occur either at the triple-phase boundary (in a composite electrode) or on the particle surface (in a mixed-conducting electrode). The incorporation and extraction of ions are accompanied by the uptake or release of electrons. Consequently, such processes are commonly referred to as charge transfer or Faradaic reactions.

For charge transfer to take place, an energy barrier must be overcome. Its height depends on the operating conditions. The hindered incorporation and extraction of ions are caused by Helmholtz double layers, which form at equilibrium due to the accumulation of charge carriers at the interfaces. With an external current, these accumulated charge carriers are removed, reducing the Helmholtz double layer and the associated energy barrier. The relationship between the

applied current density and the activation overpotential $\eta_{\text{act,EL}}$ is highly non-linear and is typically modeled using the Butler-Volmer equation (80, 91, 92, 93):

$$j = j_{0,\text{EL}} \cdot \left[\exp \left(\frac{\alpha_{\text{EL}} z F \eta_{\text{act,EL}}}{R_g T} \right) - \exp \left(\frac{-(1 - \alpha_{\text{EL}}) z F \eta_{\text{act,EL}}}{R_g T} \right) \right], \quad (2.32)$$

where $\eta_{\text{act,EL}}$ is the activation overpotential, F is the Faraday constant, R_g the universal gas constant, T the temperature, z the number of electrons involved (anode: $z = 2$, cathode: $z = 4$), and $\alpha_{\text{EL}} \in (0, 1)$ is the symmetry factor describing the polarization behavior of the electrode.

The reaction kinetics dependence on operating conditions is incorporated into the Butler-Volmer model through the exchange current density $j_{0,\text{EL}}$, which is semi-empirically determined for both electrodes (69, 94):

$$j_{0,\text{An}} = \gamma_{\text{An}} \cdot (p_{\text{H}_2,\text{An}})^a \cdot (p_{\text{H}_2\text{O},\text{An}})^b \cdot \exp \left(\frac{-E_{\text{act,An}}}{R_g T} \right), \quad (2.33)$$

$$j_{0,\text{Cath}} = \gamma_{\text{Cath}} \cdot (p_{\text{O}_2,\text{Cath}})^m \cdot \exp \left(\frac{-E_{\text{act,Cath}}}{R_g T} \right), \quad (2.34)$$

The exchange current density $j_{0,\text{EL}}$ is a measure of the catalytic activity of the electrode. $E_{\text{act,EL}}$ is the activation energy, γ_{EL} the pre-factor, and a, b, m are exponents specific to the electrode material and its manufacturing process. The partial pressures p_i of the relevant gas components are included to account for concentration effects on charge transfer.

2.3.3.1 Comparison of Reaction Mechanisms in Ni/YSZ and Ni/GDC Anodes

The point where Ni, YSZ, and pores connect, the TPB, is the site of the electrochemical reaction. A schematic of a Ni/YSZ anode during SOFC operation is shown in Figure 2.3. At the TPB, oxygen ions from the YSZ react with hydrogen diffusing through the pore, releasing electrons that are transported via the percolated Ni phase to the external circuit. The steam produced is transported simultaneously from the electrode through the pores. Therefore, Ni / YSZ anodes are designed to maximize the number of reaction sites, i.e., to achieve a high TPB density (95, 96).

Despite this design strategy, Ni/YSZ cermet fuel electrodes face significant performance limitations at lower operating temperatures. The ionic conductivity of YSZ is insufficient for operation at these temperatures (98). Moreover, Ni/YSZ anodes are not resistant to sulfur poisoning, given the presence of sulfur compounds in many fuel sources (99, 100). Even minimal H_2S

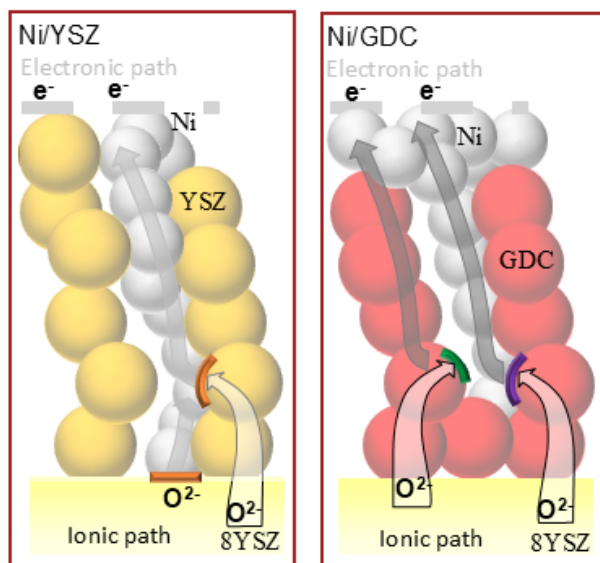


Figure 2.3: Schematic drawing of the electrochemistry of the Ni/YSZ (left) and Ni/GDC (right) electrodes. The charge transfer at the double-phase boundary is colored green; the reaction at the TPB between Ni, GDC, and the gas phase is purple, and between Ni, YSZ, and the gas phase is orange. Adapted from (97).

exposure (less than 1 ppm) caused a five-fold increase in the polarization resistance of Ni/YSZ anodes (101, 102). The degradation is attributed to sulfur absorption on the Ni surface, reducing its catalytic effectiveness for hydrogen electro-oxidation at the TPB or for the water-gas shift reaction (101, 17).

In contrast, Ni/ceria anodes exhibit superior ionic conductivity and sulfur tolerance. At temperatures as low as 500 °C, GDC exhibits significantly higher ionic conductivity than YSZ (103). The improved sulfur resistance originates largely from GDC's MIEC, allowing reactions to occur not only at the TPB but also at the GDC-pore interfaces (18, 104). As illustrated in Figure 2.3, reactions can take place directly on the GDC surface, with electrons transported to the external circuit through the electronically conducting GDC phase, without the need for a continuous Ni network.

2.4 Approaches for Low-Temperature Performance Enhancement

Operating SOFCs at temperatures below 650 °C broadens the range of accessible, cost-effective materials and enhances overall system stability. However, performance typically declines at lower temperatures due to the low ionic conductivity of conventional electrolytes, such as YSZ, which increases ohmic resistance. Additionally, the electrode polarization resistance increases because electrochemical processes are thermally activated (105). Achieving superior performance and stability at intermediate temperatures, therefore, requires the development of novel materials and innovative fabrication techniques (103).

2.4.1 Nanoscience and Nanotechnology

Nanoscience and nanotechnology have become powerful tools for overcoming low-temperature limitations by modifying material properties at the nanoscale. Recent research has explored a variety of approaches to engineer high-performance nano-structured SOFC components. The unique features of nanomaterials, such as high surface area, enhanced defect chemistry, and tunable morphologies, offer great potential to improve grain-boundary ionic conductivity in electrolytes and enhance reaction kinetics at electrode interfaces.

Arico et al. (106) provided a comprehensive review of nano-structured materials in energy-related applications, including low-temperature fuel cells, hydrogen storage, fuel reforming, and catalyst development. Nano-structured ceria-based powders such as GDC, YDC, SDC and YSZ have been reported to lower sintering temperatures due to their distinct sintering behavior. Nano-sized ceria further optimizes electrode-electrolyte charge transfer due to its mixed-ionic–electronic conductivity. This behavior originates from point defects that act as ionic charge carriers in electroceramics. Yuan et al. (107) highlighted the importance of controlled synthesis of Ce-based nanomaterials. Important factors are crystal orientation, particle size, and shape, which significantly affect material properties. Dong et al. (108) synthesized nano-sized Ce-based electrolytes using a polyvinyl alcohol-assisted combustion method, yielding cubic fluorite structures with porous foamy morphology. Bellino et al. (109) prepared cobaltite nanotube cathodes exhibiting low polarization resistance and high porosity.

2.4.2 Advanced Fabrication Techniques

Advanced fabrication techniques are essential in improving SOFC performance by enabling precise control of microstructure and optimizing electrode/electrolyte interfaces. Recent studies reveal various nanoengineering strategies that significantly influence catalytic activity, morphology, and overall cell efficiency.

Yoon et al. (110) developed vertically aligned nanocomposite thin films on top of GDC electrolytes and LSCO cathodes, achieving enhanced efficiency gains in thin-film SOFCs. Evans et al. (111) fabricated porous cathodes using spin-coating of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ nanoparticles and salt-assisted spray pyrolysis, resulting in structures suitable for integration with electrolytes. Guan et al. (112) employed X-ray nano-tomography to investigate 3D porous Ni-YSZ anode structures, revealing their intricate morphology.

Pelegrini et al. (113) discussed nanostructured Ni/Cu-YSZ materials for increasing TPB density and electrochemical activity on the anode side. Kwon et al. (114) synthesized Co–Ni alloy nanoparticles and double-layered perovskites $\text{PrBaMn}_{1.7}\text{Co}_{0.1}\text{Ni}_{0.2}\text{O}_{5+\delta}$ to improve catalytic activity. Cavallaro et al. (115) studied the deposition of dense $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ films via PLD and the strong effect of deposition temperature on film morphology and oxygen diffusion.

2.4.3 Nanoparticles Infiltration Methods

Infiltration is another widely used approach to introduce nanoparticles into porous anode backbones, thereby suppressing sulfur poisoning, enhancing coking resistance, and increasing TPB density. These improvements are crucial for electrochemical reactions at the electrode-electrolyte interface (116, 117). However, the long-term effectiveness can be limited by phase coarsening and reduced percolation of nanoscale catalyst phases (118, 119).

Recent research has focused on infiltration in percolated Ni/YSZ cermet scaffolds. By doping GDC to form an MIEC phase, electronic transport is improved, and effective utilization of the additional TPBs formed is ensured (116, 120, 121). Boldrin et al. (122) stated that Ni nitrate infiltration into GDC scaffolds produced anodes with excellent low-temperature performance ($<700^\circ\text{C}$) in H_2 and syngas. A prior study from our group (17) investigated various Ni/ceria cermet anodes. An electrode of a Ni/GDC layer directly screen-printed on 8YSZ exhibited notable initial polarization resistance. However, sulfur exposure significantly increased polarization resistance. This drawback was successfully addressed by infiltration with a Ni and/or ceria solution, reducing the initial polarization resistance to below $200\text{ m}\Omega\text{cm}^2$.

Mitchell-Williams et al. (123) applied inkjet printing to infiltrate GDC particles into commercially available NiO-8YSZ|8YSZ|LSCF anode-supported cells. At 600 °C, this reduced polarization resistance and improved aging resistance. Additional studies of Ni infiltration into pre-sintered YSZ or CeO₂-based structures confirmed that relatively low nanoparticle loadings maintained adequate electronic conductivity (124, 125). In contrast, infiltration of GDC into pure Ni anodes yielded inconsistent results (126, 127, 128, 123, 129).

Overall, nanoscience and advanced material engineering provide effective strategies to overcome low-temperature performance limitations in SOFCs. At FZJ, several of these techniques, including nanoparticle use, infiltration, and traditional screen printing, are employed to fabricate Ni/GDC electrodes for symmetrical cells. The electrochemical characterization and operational testing of these electrodes are fundamental aspects of this work.

2.5 Degradation Mechanisms

In this study, we focus exclusively on degradation at the cell level, specifically in cells with an 8YSZ electrolyte and symmetrical Ni/GDC fuel electrodes. Consequently, stack-level issues, such as degradation of interconnects and sealants, are not included.

The degradation of SOFCs is commonly classified into two categories:

- **Intrinsic factors:** originating from internal sources, such as microstructural changes, fractures, and delamination.
- **Extrinsic factors:** resulting from external influences, including reactions with fuel components and environmental conditions.

For this dissertation, all cells were operated using laboratory-level hydrogen, oxygen and inert gases. Typical contaminants in fuel gas, such as sulfur, were therefore not considered. This section will focus on intrinsic degradation mechanisms affecting Ni/cermet anodes (Ni/YSZ and Ni/GDC).

2.5.1 Overview of Degradation in Electrolyte and Cathode

Electrolyte

In SOFCs, the electrolyte is a critical component whose degradation over time significantly affects the overall performance of the cell. Several studies have highlighted the importance of electrolyte stability and the factors contributing to its deterioration. For example, the ionic conductivity of electrolytes containing 8–10 mol% Y_2O_3 in ZrO_2 is reported to decrease with operation time (130). This reduction is often attributed to a cubic-to-tetragonal phase transition (131). The degradation rate is highest during the first 1000 h of operation at 950–1000 °C, with conductivity losses up to 25% (132).

Another factor influencing 8YSZ conductivity is Ni contamination, which originates from NiO diffusion into the electrolyte during co-sintering, followed by its reduction and exsolution as metallic Ni under reducing conditions (133).

Cathode

Perovskite-based cathode materials containing lanthanum, barium, and strontium are widely used in SOFCs. However, these cathodes are susceptible to degradation from corrosive agents such as CO_2 , moisture, silicon, sulfur, and chromium. The mechanisms of poisoning vary among cathode materials. They all lead to a reduction in electrochemical performance, as analyzed by various characterization methods (134). Common degradation indicators applied for cathode materials include voltage drops, increased non-ohmic resistance (135), and poisoning by silicon and chromium (136, 137).

CO_2 primarily strengthens the formation of carbonate phases on the cathode surface, reducing oxygen adsorption (138). Attempts to suppress this effect, such as silicon incorporation, can induce Si poisoning (139). Moisture does not directly deactivate reaction sites but can degrade cathodes depending on their composition (140, 141, 136, 142, 143).

Specifically, silicon poisoning results in the formation of silicate layers at nucleation sites, thereby reducing oxygen exchange efficiency (144). Sulfur poisoning produces sulfite ions that occupy oxide ion vacancies, increasing polarization resistance (145, 146). Volatile strontium compounds similarly decrease performance, and chromium poisoning, mainly originating from interconnects, remains a critical field of research for mitigation strategies (147, 126, 148, 149).

Intrinsic degradation mechanisms, such as cation interdiffusion, localized densification, and compound formation, are also significant. La-based cathodes often degrade via coarsening and Sr

segregation, whereas LSC electrodes display higher stability (150). Boron-induced microstructure degradation has been observed but not intensively studied. Ba-based cathodes may undergo structural disintegration under operational temperature fluctuations, leading to reduced oxygen transport (151).

2.5.2 Degradation in SOFC Anode

2.5.2.1 Ni Agglomeration

One of the most frequently reported degradation phenomena in Ni/cermet anodes is Ni coarsening. This process involves agglomeration of Ni particles, loss of Ni–Ni contact, and changes in the surface morphology of grains (152, 153, 154, 155). Two mechanisms are generally considered responsible for this phenomenon:

1. particle sintering driven by diffusion processes (156)
2. transport of volatile Ni species through the gas phase (157).

Both mechanisms depend strongly on operating conditions, particularly load, temperature, and humidity.

Sintering of Ni particles at elevated temperatures is driven by particle-related properties such as size, curvature, and surface energy. Smaller particles have higher surface energy, which intensifies agglomeration to reduce the system energy (158). Vaßen et al. (156) introduced a "two-particle model" based on the ripening effect, considering the curvature of neighboring particles. In this model, differences in gas pressures near particles with different sizes induce a diffusive vacancy flux, leading to particle coarsening.

For the anode, the increase in Ni particle size reduces the TPB length, leading to an increase in the polarization resistance (159) and decreases in electrical conductivity due to loss of Ni–Ni contact (160). Studies show that Ni degradation is accelerated in humid atmospheres. For example, Holzer et al. (26) reported a Ni growth rate of 2.8%/h for a 40% Ni - 60% GDC compound in long-term operation that lasted more than 1000 hours. Similarly, Simwonis et al. (153) observed a 33% reduction in conductivity of Ni/YSZ cermet after 4000 hours at 1000°C under Ar/4% H₂/3% H₂O/93%.

Ni coarsening due to the formation of Ni(OH)₂ is another significant mechanism (161). The formation of volatile Ni(OH)₂ leads to Ni loss from the anode (153, 154, 162). In H₂/H₂O environments, Ni(OH)₂ is the most volatile and stable Ni species based on thermodynamic data,

with its partial pressure approximately six times higher than other gaseous species (157). At elevated temperatures like 900-1000 °C, small amount of water vapor (1-2%) is sufficient to form $\text{Ni}(\text{OH})_2$ (26). The gaseous $\text{Ni}(\text{OH})_2$ migrates to low-humidity regions and decomposes back to Ni particles, preferentially from smaller to larger grains. This redistribution of Ni explains both Ni grain growth and Ni loss in certain anode areas. For instance, Hagen et al. (154) reported a 40% Ni loss in a 1 cm^2 area after 1500 hours under humidified hydrogen at 1.9 A/cm^2 . The particle size distribution shifted towards a larger grain size. Matsui et al. (162) observed a decrease in Ni volume fraction from 25.3% to 23.6% at 1000°C, with TPB length reducing from 2.49 to $1.68 \mu\text{m}^2$ and Ni particle size increasing from 1.38 to $1.75 \mu\text{m}$ after 48 hours. In the publication of Sciazko (163), both Ni/GDC and Ni/YSZ electrodes exhibited Ni coarsening during SOEC and SOFC operation.

2.5.2.2 Redox Instability

A continuous supply of fuel is essential for sustained SOFC operation without damaging the anode. With an interruption in fuel supply, the O^{2-} ions traveling to the anode can cause oxidation of Ni to NiO. Similarly, NiO can form if fuel utilization or the partial pressure of H_2O on the anode side increases. This oxidation is accompanied by a 69.9% increase in volume (164). This phenomenon, redox cycling, is a major cause of stress accumulation, which decreases electrochemical performance by reducing TPB density and eventually leads to mechanical failure (165, 166, 167, 168, 169, 170).

A detailed study by Klemensø et al. (165) showed that the particles were uniform in NiO and YSZ after the initial sintering. After reduction, NiO was converted to Ni, resulting in a 25% volume decrease. Ni grain growth was observed after long-term sintering/operation. Reoxidation of the grains led to volume mismatches compared to the initial sintered state, inducing local stresses. These stresses led to additional porosity, network distortions, and eventually cracks in the electrolyte. Malzbender et al. (171) observed that the crack density increased after the oxidation–reduction cycle was carried out twice on a NiO/YSZ anode (165).

Anodes with fine microstructure show cracks after reoxidation, while anodes with coarser microstructure do not exhibit such behavior (172). This phenomenon has been attributed to the porosity percentage of the samples. Higher temperatures and high $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ ratios also strengthen redox-induced degradation (165, 170).

2.5.2.3 Ni Depletion

Several studies have shown that long-term degradation of Ni/YSZ cermets with Ni coarsening can lead to Ni migration from the functional layer to the contact layer, a major cause of performance loss (173, 174, 175). Yokokawa et al. (176) suggested that Ni transport occurs via evaporation/condensation and diffusion mechanisms, especially under high temperature and high water partial pressure conditions. Ni(OH)₂ formation near TPBs, enhanced by high current densities and water content, accelerates this degradation.

Barfod et al. (177) reported that Ni depletion increases with higher current. The elevated steam partial pressure promotes Ni(OH)₂ formation and redistribution within the anode. Sezer et al. (178) simulated Ni migration under different wet/dry and current conditions ($I = 250 \text{ mA/cm}^2$ vs OCV), suggesting movement from the electrolyte interface toward the anode surface. Similarly, Celik et al. (179) found that both applied current and steam concentration accelerated Ni transport to the anode surface. Steam concentration also directly affects the formation of secondary phases (179, 180, 181).

Trini et al. (182) reported that while Ni coarsening is largely independent of the operation mode, Ni migration occurs exclusively under SOEC conditions. This was attributed to differences in contact angle arising from the wetting behavior. Jiao et al. (183) further investigated the effect of operation mode on Ni-patterned electrodes, revealing that wettability is reduced during electrolysis compared to fuel cell operation, which can lead to Ni delamination. The same was observed by Sciazko (163). A clear Ni-free layer 2 μm thick was observed near the electrode/electrolyte interface after 100 h of operation in SOEC mode. This depletion was not observed in the electrode operated under the same conditions with the current flowing in the opposite direction.

2.5.2.4 GDC Agglomeration

Compared to the commonly stable zirconia matrix, microstructural changes in the GDC phase have been observed and reported (26, 27, 28). Holzer (26) reported the quantitative evolution of the particle size of Ni, pores, and GDC under various operating conditions, showing that the growth of all particles was accelerated by temperature and humidity. Uecker et al. (184) found that after 1200 h of testing of a pure GDC fuel electrode, particle coarsening led to densification of the pore structure. Remarkably, the grain size increased by more than 100%.

In this work, a clear sintering effect in the fine GDC structure was observed. The strong agglomeration of GDC particles at elevated temperatures, accompanied by potential electrode reorganization, is a key factor in designing the accelerated stress testing protocol.

2.5.2.5 GDC Coating

Another degradation phenomenon is the formation of a GDC coat on Ni surfaces after long-term operation (15,000 h) (26, 27). Although this coating can prevent Ni coarsening, it also hinders mass transport, reducing both TPB length and Ni percolation. Kubota et al. (185) investigated the interaction of ceria with Ni surfaces and suggested migration of CeO_2 species over Ni under reducing conditions.

The group of Sciazko extensively studied microstructural changes in Ni/GDC electrodes (186, 187, 163), revealing that GDC nanoparticles migrated several micrometers to form a thin layer on Ni surfaces, resembling strong metal-support interaction. This phenomenon was most intense near the current collector and during SOEC operation. This is often accompanied by Ni intrusions into GDC grains due to electrochemical interactions (163). Over 51 h of operation, both Ni and GDC dynamically migrated over tens of microns, changing the TPB length. GDC nanoparticles accumulated on Ni surfaces, and the surface of the GDC became rougher, indicating a significant morphological evolution (186).

2.6 Accelerated Stress Testing for Lifetime Prediction

In this section, the methodology of accelerated stress testing is introduced, and its applicability to SOFCs is discussed, both in general and in the framework of this work. The discussion begins with selected aspects of reliability theory for a conceptual foundation. Subsequently, the general concept of calendar life prediction, combined with several widely used aging models in engineering, is introduced. The AST, as a powerful tool, enables researchers to predict long-term performance within a reasonable time frame. In this work, the equivalent time concept based on AST, commonly used in materials science and nano electronics for equivalent degradation analysis, is adapted to SOFC electrodes. Moreover, carefully designed experimental setups or analytical separation techniques are essential, as competing failure mechanisms may distort lifetime predictions.

2.6.1 Quantification of Aging in a Single Cell

The degradation of the performance of a single SOFC cell can be evaluated as a decrease in the electrical power density P or as an increase in the ASR over operation time. The time derivative of these parameters defines the degradation rate. For researchers, the behavior of the internal

resistance is of particular interest because it directly reflects the system's physical changes. For the user, only the available power density is relevant, with its degradation expressed as (188):

$$\frac{dP}{dt} = \frac{d}{dt} [U_{\text{cell}} \cdot j_L] = \frac{d}{dt} [(U_N - j_L \cdot ASR) \cdot j_L] \quad (2.35)$$

Under constant load current j_L , the electromotive force U_N remains constant. Hence, the time derivatives of both quantities vanish, resulting in the following relationship for the degradation rates of power and resistance:

$$\frac{dP}{dt} = -j_L^2 \frac{dASR}{dt} \quad (\text{for constant } j_L) \quad (2.36)$$

It is also common to specify normalized degradation rates, e.g., 1% per 1000 h, which correspond to derivatives relative to the respective quantity. For constant current operation, the normalized degradation rate of power density can be expressed as (188):

$$\frac{1}{P} \cdot \frac{dP}{dt} = \left(1 - \frac{U_N}{ASR \cdot j_L}\right)^{-1} \cdot \frac{1}{ASR} \cdot \frac{dASR}{dt} \quad (2.37)$$

With D_P and D_{ASR} representing the normalized degradation rate, the last equation is simplified to:

$$D_P = \frac{1}{1 - \frac{U_N}{ASR \cdot j_L}} \cdot D_{ASR} \quad (\text{for constant } j_L) \quad (2.38)$$

Equation (2.38) indicates that, for known ASR aging, the degradation rate of the power at a constant current operating point is derivable. It can be seen that for fixed D_{ASR} , the power degradation D_P increases strongly with increasing load current density j_L . An asymptote occurs at very high current densities, as the cell voltage U_{cell} approaches zero when $j_L \rightarrow U_N/ASR$.

Under the simplifying assumption that U_N remains constant during aging, a relation for the normalized power degradation rate can be derived (188):

$$\frac{1}{P} \frac{dP}{dt} = \frac{1}{ASR} \cdot \frac{dASR}{dt} \quad (2.39)$$

2.6.2 Calendar Life Prediction

The lifetime of a component is defined as the period from initial use until it no longer meets specified performance or functionality requirements. While this definition is straightforward for devices with abrupt failure, such as incandescent bulbs, high-temperature SOFCs typically exhibit a gradual performance decline, referred to as degradation. In such cases, a different definition of failure is employed: a component is considered failed when its performance drops below a predefined threshold (189). This threshold is determined commercially based on factors such as cell count, operating point, and warranty requirements.

In reliability theory, the time to failure is described by a random variable characterized by a failure density $f(t)$ and a distribution function $F(t)$. Commonly used distributions include the Weibull, normal, and log-normal distributions. In particular, the distribution function introduced by Weibull in 1951 (190) has been widely adopted in lifetime studies. The well-known "bathtub curve" is, in fact, a superposition of three Weibull distributions.

In electrochemical research, various physical variables can serve as failure thresholds, including cell voltage, power density, and *ASR*. Classical lifetime testing involves operating multiple components under nominal conditions until failure, followed by fitting a statistical distribution to the resulting data to extract lifetime metrics. Typically, three to ten tests are required for a reliable fit, making conventional testing costly and time-consuming, particularly for long-lived products. Even with techniques like censoring, reducing test duration remains challenging (191).

For SOFCs, expected lifetimes range from 8,000 h in mobile power units to 80,000 h in combined heat and power systems. Therefore, predictive approaches are essential. These methods are generally divided into model-based and data-driven approaches (192).

Model-based strategies aim to explain degradation through physical or mechanistic theories. Several studies have focused on the degradation mechanisms of Ni/YSZ anodes, with key mechanisms including Ni agglomeration and loss of TPB density. For example, Wu et al. (193) developed a voltage mechanism model for Ni coarsening and oxidative degradation to estimate the remaining useful life (RUL) of SOFCs. Khan et al. (22) proposed simplified empirical models linking the increase in particle size to the reduction in TPB length, as shown in Equation 2.40:

$$L_{v(\text{TPB})}(t, T) = 2\pi a \frac{\bar{r}_{\text{Ni},i}^2}{\bar{r}_{\text{Ni},t}^2} + C \quad (2.40)$$

$L_{v(\text{TPB})}$ denotes the experimental volumetric triple phase boundary length, $\bar{r}_{\text{Ni},i}$ the initial Ni particle size and $\bar{r}_{\text{Ni},t}$ the Ni particle size after operation time of t . The fitting parameters a and

C were obtained from regression analysis. Furthermore, the polarization resistance of the anode, $R_{\text{pol}}(t)$, can be expressed as a function of $L_{\text{v(TPB)}}(t)$ according to Equation 2.41:

$$R_{\text{pol}}(t) = \frac{R_{\text{TPB}}}{L_{\text{v(TPB)}}(t)} \quad (2.41)$$

where R_{TPB} denotes the intrinsic charge-transfer resistance per unit TPB length. Microstructural models have also quantitatively described the degradation of Ni percolation probability, effective TPB area, and effective conductivity over time (194, 195).

Although these approaches offer advantages such as lower data requirements and high accuracy (192), their application to Ni/GDC anodes remains challenging. Unlike the stable YSZ matrix, the GDC phase is mobile and can wet Ni surfaces (27, 28), complicating the prediction of Ni agglomeration and TPB loss. Moreover, Ni was shown to act as a catalyst on the GDC surface, introducing complex dependencies between charge-transfer resistance and microstructural parameters (79). Kullmann (78) investigated Ni-infiltrated GDC electrodes and compared the activation energy of charge-transfer resistance r_{ct} with that of pure GDC electrodes. With increasing Ni loading, the activation energy decreased from 95 to 85 kJ/mol. These values are significantly lower than those typically reported for conventional screen-printed Ni/GDC electrodes targeting elevated temperatures (196). This difference suggests a fundamental difference in the underlying reaction mechanism. It can be assumed that, as Ni particles agglomerate, a critical threshold exists beyond which a transition in the dominant reaction mechanism occurs.

This complexity underlines the limitations of pure mechanistic models and highlights the necessity of complementary data-driven approaches. They are capable of capturing such non-linear and transitional behaviors without previously defining the physical boundary conditions. These approaches analyze SOFC degradation trends using historical data (192), and previous studies have applied Artificial Neural Networks (ANNs) to predict SOFC voltage under various conditions (197, 198). However, voltage alone is often an unreliable indicator of degradation, as it is sensitive to multiple external factors (199). Instead, ASR serves as a more reliable indicator for degradation. In this work, symmetrical cells are employed to exclude cathode processes or processes at the air electrode, thereby simplifying impedance analysis. As all measurements are performed under OCV, the ASR or the corresponding fitted parameters, such as r_{ct} , provide the most representative indicator of the cell's degradation state.

2.6.3 Empirical Models for ASR Degradation in SOFCs

In data-driven approaches, the degradation of SOFC performance is often quantified via the increase in ASR over time. Empirical functions are widely used to fit experimental data and to extrapolate long-term behavior. The most common forms include linear, power-law, exponential, and logarithmic growth models, each reflecting different underlying degradation dynamics.

- **Linear increase:** The linear model assumes a constant rate of ASR increase:

$$ASR(t) = ASR_0 + k t, \quad (2.42)$$

where ASR_0 is the initial resistance, k is a constant degradation rate, and t is operating time. This simple model is appropriate when a single degradation mechanism dominates under steady-state conditions. For example, Nakajo et al. (2000) observed nearly linear ASR growth in the cathode of the Ni/YSZ anode-supported cells under constant current and temperature, indicating that linear extrapolation can reliably estimate mid-term lifetime in such cases. Cui et al. (192) proposed a dynamic model for SOFC degradation based on ASR changing linearly over time.

- **Power-law function:** The power-law model captures sublinear growth, where the degradation rate slows with time:

$$ASR(t) = ASR_0 + c t^n, \quad 0 < n < 1, \quad (2.43)$$

with c as a scaling coefficient and n as the power-law exponent. This form is widely used in materials science and fuel cell research to describe degradation that is rapid initially but gradually decelerates. In Ni/YSZ electrodes, the polarization resistance is directly linked to the TPB and, therefore, to the Ni particle size. Ni particle growth is commonly described using a power-law model, which, in turn, generally results in a corresponding power-law behavior for the temporal evolution of the polarization resistance, as presented in (22, 195, 201).

- **Exponential function:** Exponential models are suitable when degradation accelerates rapidly, for example, at elevated temperatures or high current densities:

$$ASR(t) = ASR_0 \exp(at), \quad (2.44)$$

where a is the exponential rate constant. This model has been applied to describe Ni particle coarsening and oxidative degradation, which can lead to strong non-linear ASR growth at high stress levels. However, this is rarely used to directly describe the evolution

of ASR , as it typically shows a decelerating increase. Instead, another form shown in the work of Hauch et al. (202) is applied:

$$ASR(t) = ASR_0 + \Delta ASR \cdot [1 - \exp(-t/\tau)], \quad (2.45)$$

where ΔASR is a fit parameter and τ is the characteristic time for the Ni/YSZ electrode degradation. Pihlatie et al. (203) chose electrical conductivity as a degradation indicator in the Ni/YSZ electrode. The measured conductivity exhibited an initial sharp decline followed by a progressively smaller decrease, which was accurately represented using a combination of two exponential functions.

- **Logarithmic growth model:** The logarithmic model describes rapid initial ASR growth followed by a slowing rate of increase:

$$ASR(t) = ASR_0 + a \ln(1 + bt), \quad (2.46)$$

where parameters a and b describe the magnitude and curvature of the function. Although this model has not been reported for SOFCs, it has been applied in fields such as semiconductors. For example, Silva et al. (204) described logarithmic degradation behavior in metal–oxide–semiconductor devices.

These empirical models offer flexibility for fitting a wide range of ASR degradation behaviors. The choice of model depends on the observed degradation pattern, the experimental time window, and the target prediction time frame. In practice, researchers often compare multiple models to determine the best fit, and combine them with statistical or data-driven techniques for uncertainty quantification (192). Furthermore, these models can serve as building blocks for advanced lifetime prediction approaches, such as the equivalent time method, which normalizes accelerated aging data to nominal operating conditions.

2.6.4 Accelerated Stress Testing

Accelerated stress testing (AST) is widely used in reliability engineering (205) to reduce experimental effort and predict the long-term performance of technical components such as SOFCs. The main principle of AST is to expose the system to stresses that exceed nominal operating conditions. This results in accelerated degradation kinetics and a reduced time to failure. AST approaches can be categorized into two main types:

1. **Qualitative ASTs:** Extreme operating conditions, such as redox cycling, fuel or air contamination, and poisoning tests, are applied to identify weak points in electrodes or stack

design and to validate durability strategies (206, 207). These tests do not provide direct lifetime predictions but are useful for structural or materials optimization.

2. **Quantitative ASTs:** Degradation-time distributions under well-designed elevated stresses are recorded. The resulting data are then analyzed using empirical or physics-based models to extrapolate expected lifetimes under nominal operating conditions (191). Quantitative ASTs are especially valuable when multiple physicochemical processes interact, making direct mechanistic interpretation difficult.

AST protocol design is complicated because of the presence of multiple aging mechanisms. The relevance of a particular failure mode under accelerated stress must be assessed carefully, as shown in Figure 2.4:

- **Mechanism A:** Dominates both accelerated and standard stress conditions, allowing reliable extrapolation.
- **Mechanism B:** Weakly dependent on stress, limiting standard lifetime but not influencing under AST conditions.
- **Mechanism C:** Only occurs at extreme stress levels, e.g., excessive anode potential triggering Ni/NiO oxidation (208). Inclusion of this mechanism in AST-based extrapolation would lead to overestimation of standard degradation rates.

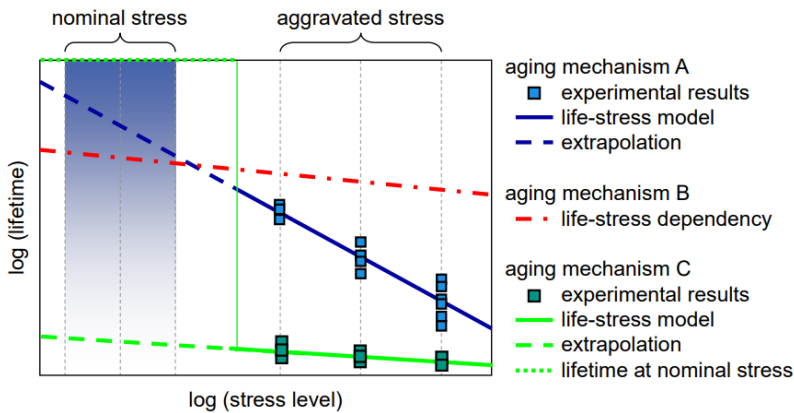


Figure 2.4: Life–stress plot presenting three different aging mechanisms. Reproduced from (208).

Thus, accelerated tests must obey material thermodynamic limits, ensuring that only mechanisms active under both standard and accelerated conditions are used for lifetime predictions. This principle has been emphasized in several SOFC studies, e.g., Diethelm et al. (206) and Weber

et al. (208), in which stress levels were carefully selected to accelerate degradation without introducing artifacts.

In this work, no real failure is defined in advance. The target is the development of a whole workflow of *ASR* prediction. The relationships between time under different stressors are discussed in terms of the common equivalent time concept (Section 2.6.5) and its extension based on an assumed Arrhenius degradation model, as illustrated in Section 4.5.

2.6.5 Equivalent Time Concept

In materials science, the equivalent degradation concept is frequently used to describe accelerated aging processes under varying environmental conditions. The key point is that the same level of degradation (e.g., an increase in resistance or a decrease in strength) can be achieved through different combinations of stressors and exposure times. This equivalence leads to the definition of an equivalent time t_{eq} , which projects accelerated testing conditions onto a reference condition.

For instance, if degradation is assumed to follow a function $y(t, T)$ that depends on both time t and temperature T , then for a fixed degradation level y^* , one can define

$$y(t, T) = y^* \iff t_{\text{eq}}(T), \quad (2.47)$$

where $t_{\text{eq}}(T)$ is the equivalent time at reference temperature T_{ref} needed to reach the same degradation level. In practice, this mapping is often constructed by normalizing degradation development to a common scale.

Wei et al. (209) developed a CMed-based optimization model for accelerated corrosion tests, selecting appropriate stress levels to ensure corrosion-mechanism equivalence and the target acceleration factor. Lyu et al. (210) investigated polylactide hydrolysis and established a time–temperature equivalence for degradation, constructing a master curve covering a 3–5 year equivalent period at 37 °C. Carino et al. (211) studied high-performance concrete with low water–cement ratios and applied the maturity method to capture time–temperature equivalence of strength development. Compressive strength data from specimens cured at 7, 23, and 40 °C were converted to equivalent ages at 23 °C, collapsing all results onto a single curve.

Although equivalent degradation analysis is rarely applied in SOFC research, it can be adapted to model performance decline under diverse operating conditions. In quantitative AST, failure times t can be recorded as a function of applied stress s . Standard acceleration laws are then applied to relate elevated-stress data to nominal operating conditions. For example, lifetime can be expressed by a power-law relationship, in which time decreases as a function of stress raised to

an empirical exponent, or by the Arrhenius law, which relates degradation rates to temperature via an activation energy. Once such models are fitted to experimental data, they enable predictions of performance and durability at nominal conditions (191).

$$t = A \cdot s^b, \quad (\text{power-law acceleration, experimentally validated}) \quad (2.48)$$

$$t = A \cdot \exp\left(\frac{E_{a,\text{age}}}{k_B T}\right), \quad (\text{Arrhenius law for elevated temperatures}) \quad (2.49)$$

where A and b are empirically fitted parameters, $E_{a,\text{age}}$ is the activation energy of aging, T the absolute temperature, and k_B the Boltzmann constant.

In this work, the equivalent time concept has been introduced to relate accelerated aging data at elevated temperatures (with varying humidity) to the long-term behavior under nominal conditions (600°C, 50% humidity in hydrogen). The equivalent time is expressed as

$$t_{\text{eq}} = \int_0^t \phi(T(\tau), p_{\text{H}_2\text{O}}(\tau), \dots) d\tau, \quad (2.50)$$

where ϕ is a transfer function accounting for the acceleration factors such as temperature, humidity, or current density. In its simplest form, ϕ can be chosen based on Arrhenius-type activation energies,

$$\phi(T) = \exp\left[-\frac{E_{a,\text{age}}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right]. \quad (2.51)$$

Using this approach, degradation data collected at high temperatures (e.g., 625–750°C) can be projected onto an equivalent timescale at 600°C. This transformation enables the prediction of long-term SOFC degradation far beyond the available experimental window. Compared to empirical functions, the equivalent time approach provides normalization that accounts for the combined influence of multiple stressors and requires no presumed degradation pattern.

Figure 4.48 in section 4.5 schematically illustrates how degradation development at different temperatures has been stretched along the time axis onto a single curve. This normalization substantially improves the robustness of lifetime prediction and offers a novel extension of data-driven methodologies for SOFCs.

2.6.6 Deconvolution of Aging Mechanisms

Accurate lifetime prediction requires more than measuring total time to failure. A detailed analysis of internal losses is essential. In SOFCs, the total cell resistance can be separated into contributions from ohmic resistance (electrolyte), charge-transfer resistance (electrodes), and mass transport limitations (208, 212). Using equivalent circuit models, such as the Gerischer element for MIEC cathodes, these contributions can be quantified and correlated with microstructural or material changes (212).

The necessity of deconvolution has been demonstrated in several studies. For example, Weber et al. (208) performed accelerated tests on Ni/YSZ anode-supported cells and successfully deconvoluted full cell resistance into electrolyte ohmic, anode charge transfer, and cathode charge transfer processes. Their observation revealed that fuel electrode degradation was strongly thermally activated, whereas air electrode aging showed a complex dependence on operating temperature and gas composition. Similarly, Endler et al. (212) associated cathode aging with changes in the chemical diffusion coefficient D_{chem} and the chemical surface exchange coefficient k_{chem} .

Symmetrical cell configurations provide a particularly powerful tool for such durability studies. They isolate single electrode behavior, eliminating cross-dependencies between anode and cathode processes (79). This makes it possible to unambiguously attribute ASR growth to a single electrode, enabling more precise quantification of degradation.

The application of combined calendar life prediction and AST is illustrated in Section 4.5.

2.7 Impedance Spectroscopy

The loss processes of a fuel cell described in Section 2.3 cannot be sufficiently distinguished in the current-voltage characteristic curve, leaving individual contributions overlapping each other. Therefore, a comprehensive understanding of the general and dominant processes is essential for predicting cell voltage (80, 81).

Using impedance spectroscopy, the dynamic behavior of electrical, physical, and electrochemical systems can be characterized. The foundation for impedance spectroscopy took place at the end of the 19th century, when Oliver Heaviside, with his considerations of electrical circuit elements and their alternating current behavior, created the basis for it (213). In 1894, Walther Nernst applied impedance spectroscopy for the first time to a physical system to determine the dielectric constants of liquid electrolytes (214). The first application of impedance spectroscopy to electrochemical systems was performed by Emil Warburg in 1899 (215). Thanks to technological advances in measurement techniques and evaluation software over the past century, impedance spectroscopy

has developed as a valuable characterization method. A historical overview of the development of impedance spectroscopy can be found in (93, 216). A more in-depth insight into the theory of impedance spectroscopy is provided in (93, 91, 217).

When applying this method, the solid oxide cell is excited at a fixed frequency f sinusoidally either via a current signal (galvanostatic) or a voltage signal (potentiostatic), and the response is measured. For galvanostatic excitation:

$$i(t) = i_0 \cdot \sin(\omega t), \quad \omega = 2\pi f \quad (2.52)$$

where i_0 denotes the signal amplitude and ω the applied angular velocity. The voltage response is then:

$$u(t, \omega) = u_0(\omega) \cdot \sin(\omega t + \varphi(\omega)) \quad (2.53)$$

where $\varphi(\omega)$ is the phase shift and $u_0(\omega)$ is the voltage amplitude, as schematically shown in Figure 2.5 (a). Small signal excitation allows linearization around the operating point (218, 219).

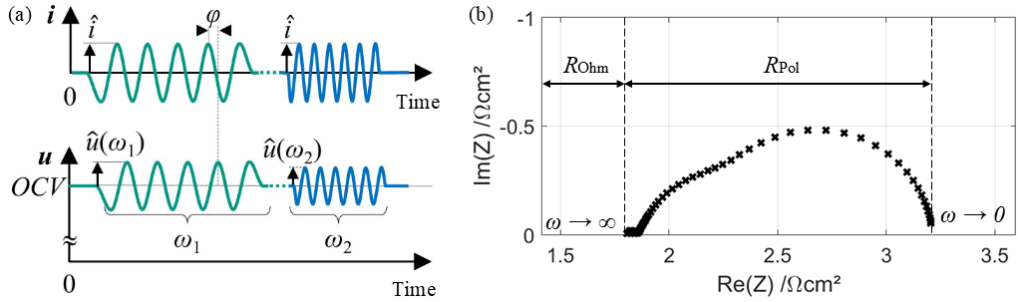


Figure 2.5: (a) Temporal progression of an EIS measurement, illustrated by the sinusoidal current excitation and the voltage response at two frequencies, ω_1 and ω_2 . Figure adapted from (65). (b) Nyquist plot of a typical impedance spectrum measured on an electrolyte-supported SOFC.

The complex impedance $Z(\omega)$ is defined as the ratio of voltage to current:

$$Z(\omega) = \frac{u(t, \omega)}{i(t)} = \frac{u_0(\omega)}{i_0} \cdot e^{j\varphi(\omega)} = Z'(\omega) + jZ''(\omega) \quad (2.54)$$

A complete impedance spectrum is recorded over a frequency range $f_{\min}$ to $f_{\max}$ and represented in a Nyquist plot (Figure 2.5 (b)). The high-frequency intersection with the real axis corresponds

to the ohmic resistance R_{Ohm} . The difference between this and the low-frequency intersection identifies the polarization resistance R_{Pol} . The evaluation assumes that the system is causal, linear, time-invariant, and finite, which is verified by the Kramers-Kronig validity test (218, 220, 221).

2.8 Equivalent Circuit Model

The goal of equivalent circuit modeling is to recreate the impedance response using analog circuit elements. Simple series connections of resistors, capacitors, and inductors are insufficient. Specialized elements are required (93, 222, 217). Physical interpretability arises when each electrochemical process is represented by an element reflecting its origin. The overall impedance is the sum of partial impedances, with parameters containing process-specific information:

- Resistance R indicates contribution to overall losses.
- Time constant τ indicates process speed.
- Impedance form reflects the physical origin of the process.

2.8.1 RQ Elements

Deviations from ideal RC behavior due to heterogeneous conditions, material variations, or manufacturing imperfections are represented by an RQ element. This element consists of a parallel combination of an ohmic resistance R and a constant phase element Q , with homogeneity factor p_{RQ} ($0 \leq p_{\text{RQ}} \leq 1$) (91, 223):

$$Z_{\text{RQ}}(\omega) = \frac{R}{1 + (j\omega\tau_{\text{RQ}})^{p_{\text{RQ}}}} \quad (2.55)$$

In Figure 2.6, the impedance curves of RQ elements are shown for different values of p_{RQ} . For $p_{\text{RQ}} = 1$, the curve corresponds to that of an RC element.

The characteristic time constant of the RQ process, i.e., the mean value of the distributed time constants, and the characteristic frequency can be calculated as (222, 223, 217):

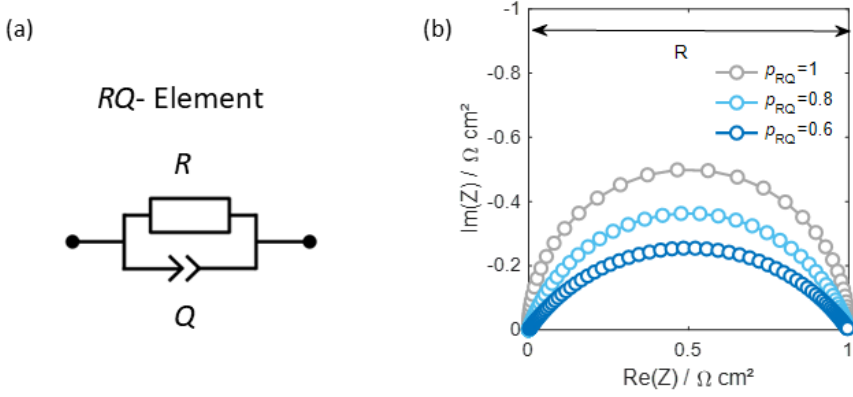


Figure 2.6: (a) Circuit symbol of an RQ element. (b) Nyquist plot of the impedance spectrum of an RQ element for $p_{RQ} = 1$ (ideal), $p_{RQ} = 0.8$, and $p_{RQ} = 0.6$.

$$\tau_{RQ} = {}^{p_{RQ}}\sqrt{R \cdot Y_0} \quad (2.56)$$

$$f_{RQ} = \frac{1}{2\pi \tau_{RQ}} \quad (2.57)$$

For the RQ element, an effective capacitance C_{RQ} can be determined, as the characteristic time constant of the RQ and RC element is identical (224, 225):

$$C_{RQ} = {}^{p_{RQ}}\sqrt{R^{1-p_{RQ}} \cdot Y_0}. \quad (2.58)$$

Rearranging and substituting into the equation representing the impedance of a constant phase element (222, 223, 217), the impedance of the CPE element within an RQ configuration as a function of the equivalent capacitance is obtained:

$$Z_{CPE,RQ}(\omega) = \frac{1}{(j\omega)^{p_{RQ}} \cdot Y_0} = \frac{R}{(j\omega R \cdot C_{RQ})^{p_{RQ}}}. \quad (2.59)$$

where Y_0 denotes general admittance parameter.

2.8.2 Gerischer Element

In mixed-conducting electrodes, the entire electrode surface is electrochemically active. From the electrode/electrolyte interface, the reaction zone extends several micrometers into the electrode volume. Both charge transport and surface exchange within this reaction zone must be taken into account. In 1996, Adler derived an analytical expression that describes this coupling (226, 227, 228):

$$Z_{\text{Gerischer}}(\omega) = \frac{R}{\sqrt{1 + j\omega \cdot \tau_{\text{Gerischer}}}}. \quad (2.60)$$

Mathematically, the impedance expression corresponds to the Gerischer element introduced by Gerischer in 1951 (226). The characteristic parameters R and $\tau_{\text{Gerischer}}$ can be calculated according to the Adler-Lane-Steele (ALS) model from thermodynamic, microstructural, and material-specific properties (227, 228):

$$R = \left(\frac{R_g \cdot T}{2 \cdot F^2} \right) \cdot \sqrt{\frac{\tau_{\text{MIEC}} \cdot \gamma_{\text{TD}}^2}{(1 - \varepsilon) \cdot a_{\text{MIEC}} \cdot c_{\text{mc}}^2 \cdot k^\delta \cdot D^\delta}}, \quad (2.61)$$

and

$$\tau_{\text{Gerischer}} = \frac{\varepsilon_{\text{MIEC}}}{a_{\text{MIEC}}} \cdot \frac{c_{\text{O}^{2-}}}{c_{\text{mc}}} \cdot \frac{1}{k^\delta}, \quad \text{with} \quad \frac{c_{\text{O}^{2-}}}{c_{\text{mc}}} = \frac{3 - \delta}{\delta}. \quad (2.62)$$

$\varepsilon_{\text{MIEC}}$, τ_{MIEC} , and a_{MIEC} represent the volume fraction, tortuosity, and electrochemically active surface area (electrode/pore interface) of the mixed-conducting phase, respectively. $c_{\text{O}^{2-}}$ is the concentration of oxygen ions, c_{mc} the concentration of available lattice sites, and δ the concentration of oxygen vacancies in the lattice. The thermodynamic factor γ^{TD} accounts for the variations in oxygen stoichiometry in the crystal lattice due to changes in oxygen partial pressure, with $\gamma^{\text{TD}} = \frac{1}{2} \frac{\partial \ln p_{\text{O}_2}}{\partial \ln c_{\text{O}^{2-}}}$.

The transport properties are described by the surface exchange coefficient k^δ and the solid-state diffusion coefficient D^δ . By rearranging Equations 2.61 and 2.62, the material properties can be directly extracted from impedance measurements.

The electrochemical penetration depth λ into the electrode volume is:

$$\lambda = \sqrt{\frac{D^\delta \cdot \varepsilon_{\text{MIEC}}}{\tau_{\text{MIEC}} \cdot a_{\text{MIEC}} \cdot k^\delta}} \quad (2.63)$$

The Gerischer element exhibits a 45° slope at high frequencies, a characteristic of solid-state diffusion, and a compressed RC-like behavior at low frequencies (Figure 2.7(a)).

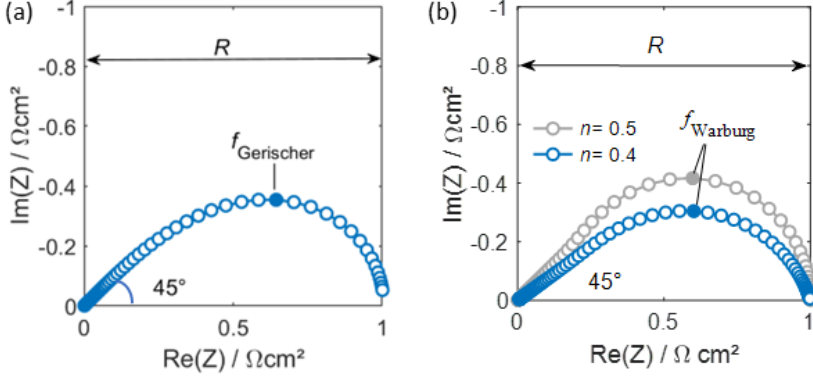


Figure 2.7: (a) Impedance behavior of the Gerischer element: high-frequency slope 45°, low-frequency RC-like behavior. (b) Nyquist-plot response of the Warburg element for $n = 0.5$ and $n = 0.4$.

2.8.3 Warburg Element

For a one-dimensional diffusion process of an electrochemically active species along a finite diffusion length L , the dynamic diffusion behavior can be described using the Finite-Length Warburg Element (FLW) (82, 229, 230, 91, 217). The original observation by Warburg (1988) (215) was based on Fick's laws (230, 222, 217).

For the diffusion in an ideal electrode, the impedance is given by:

$$Z_{\text{Warburg, ideal}}(\omega) = R \cdot \frac{\tanh\left(\sqrt{j\omega \tau_{\text{Warburg, ideal}}}\right)}{\sqrt{j\omega \tau_{\text{Warburg, ideal}}}} \quad (2.64)$$

This produces the characteristic “mouse-like” curve in a Nyquist plot (Figure 2.7(b)), exhibiting a constant 45° slope ($\pi/4$) at high frequencies.

The Warburg element corresponds to a ladder-network (transmission-line) model that accounts for the capacitive pore volume. In the case of ideal one-dimensional gas diffusion, the time constant $\tau_{\text{Warburg, ideal}}$ of the Warburg element can be calculated according to Equation 2.65. In this expression, the differential resistance $r = R/L$ corresponds to the diffusion resistance per unit volume, and the differential capacitance $c = C/L$ represents the capacitive pore volume per

unit volume. The relationship between these differential quantities in the transmission line model is given through the time constant as follows:

$$\tau_{\text{Warburg, ideal}} = r \cdot c \cdot L^2 \quad (2.65)$$

Taking into account the real electrode structures, the Generalized Finite-Length Warburg (GFLW) element is applied:

$$Z_{\text{Warburg}}(\omega) = R \cdot \frac{\tanh(j\omega \cdot \tau_{\text{Warburg}})^n}{(j\omega \cdot \tau_{\text{Warburg}})^n}, \quad \text{with } 0 \leq n \leq 0.5. \quad (2.66)$$

The homogeneity factor n represents a compression of the impedance response, similar to the case of an RQ element (see Figure 2.7(b), $n = 0.4$). For $n = 0.5$, the impedance expression corresponds to that of the ideal finite-length Warburg element.

The characteristic frequency is approximated as:

$$f_{\text{Warburg}} = \frac{2.53}{2\pi \tau_{\text{Warburg}}} \quad (2.67)$$

2.8.4 Transmission Line Model

In porous electrodes, the interfaces, or triple-phase boundaries, are spatially distributed throughout the electrode volume, so that electrochemical mechanisms occur within an extended reaction zone. Within this, the (i) electronic transport, (ii) oxygen ionic transport, and (iii) gas transport are coupled through the (iv) charge transfer reaction. The modeling of reaction and transport processes in such an electrode is typically performed using transmission line models (TLM) (231, 222, 217). The segments of the "line" represent the transport paths, which are interconnected by the "rungs" of the ladder. In the model, each "rung" represents the coupling reaction between the transport pathways, as shown in Figure 2.8(a).

Over the past decades, several SOFC electrode models based on such ladder structures have been developed. The best-known TLM with physical significance is the Gerischer element, introduced by Adler for porous, single-phase, mixed-conducting cathode materials (227, 228). In his approach, the coupling of diffusive ionic transport in the solid and surface oxygen exchange was considered the dominant loss process, while electronic conduction in the solid was assumed to be ideal. More complex TLMs have been applied to Ni/cermet anodes (232, 233, 234, 235, 236).

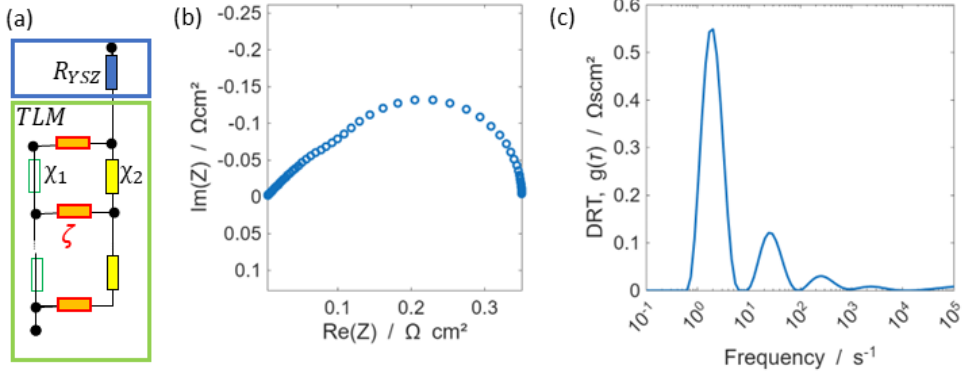


Figure 2.8: (a) Electrolyte with series connection of infinitesimal TLM elements representing a complete electrode. The TLM accounts for ionic transport in the GDC matrix (χ_2), electronic transport in the Ni (and GDC) matrix (χ_1), and the coupling of both transport pathways through the charge transfer reaction at the reaction site (ζ). An example of the (b) impedance and (c) corresponding distribution of relaxation time based on a TLM.

In these models, the penetration depth λ denotes the position within the electrode at which 63% of the current transitions from ionic to electronic pathways.

The electrochemical behavior of a homogeneous, porous electrode with layer thickness d can be analytically described by the following impedance function (231, 237, 216, 236):

$$Z_{TLM}(\omega) = \frac{\chi_1 \cdot \chi_2}{\chi_1 + \chi_2} \cdot \left(d + \frac{2 \cdot \kappa}{\sinh(d/\kappa)} \right) + \kappa \cdot \frac{\chi_1^2 + \chi_2^2}{\chi_1 + \chi_2} \cdot \coth\left(\frac{d}{\kappa}\right) \quad (2.68)$$

The variable κ is defined as the square root of the ratio of the charge-transfer resistance to the sum of the ionic and electronic path resistances:

$$\kappa = \sqrt{\frac{\zeta}{\chi_1 + \chi_2}} \quad (2.69)$$

Here, χ_1 and χ_2 represent the electronic and ionic resistances per unit length ($\Omega \text{ m}^{-1}$), and ζ denotes the charge-transfer resistance between the two paths ($\Omega \text{ m}$) with the following expression:

$$\zeta(\omega) = \frac{r_{ct}}{1 + (j\omega \cdot \tau_{ct})^n} \quad (2.70)$$

It should be noted that more complex models that consider the individual kinetic steps of charge-transfer reactions could also be applied. In this work, however, the simple use of an RC element ($n = 1$) is sufficient to achieve excellent agreement between the measurements and the model.

The validity of this TLM approach and the corresponding simulation results requires that the penetration depth λ is larger than the particle size ps of the porous microstructure ($ps < \lambda < d$), and (ii) the contribution of the diffusion path is negligible. In electrolyte-supported cells, the gas diffusion process is comparatively small due to the minor electrode thickness compared to anode-supported cells (196, 238). As gas diffusion does not limit the electrode performance, it is neglected, simplifying the complete three-channel TLM presented in (65) to a two-channel TLM (79).

Based on this general framework, we now adapt the TLM to describe Ni/GDC composite electrodes, where the degree of Ni percolation plays a crucial role in determining electronic transport. Nenning (239) adapted the Adler-type TLM, with two parallel pathways for ion and electron conduction. The local overpotential η drives the oxygen exchange reaction, represented by resistor r_{ct} and capacitor C_{ct} . The ionic and electronic resistances are expressed as:

$$R_{ion,GDC} = \frac{1}{\sigma_{eff,ion}} = \frac{\tau_{GDC}}{\varepsilon_{GDC}\sigma_{i,GDC}} \quad (2.71)$$

$$R_{eon,GDC} = \frac{1}{\sigma_{eff,eon,GDC}} = \frac{\tau_{GDC}}{\varepsilon_{GDC}\sigma_{e,GDC}} \quad (2.72)$$

$$R_{eon,Ni} = \frac{1}{\sigma_{eff,eon,Ni}} = \frac{\tau_{Ni}}{\varepsilon_{Ni}\sigma_{e,Ni}} \quad (2.73)$$

where $R_{ion,GDC}$, $R_{eon,GDC}$ and $R_{eon,Ni}$ denote the effective ionic resistance in GDC, the effective electronic resistance in GDC, and the effective electronic resistance in Ni, respectively. They can be used to parameterize χ_1 and χ_2 in equation 2.68. The terms $\sigma_{eff,ion}$, $\sigma_{eff,eon,GDC}$, and $\sigma_{eff,eon,Ni}$ represent the effective ionic and electronic conductivities of the respective phases. The parameters $\sigma_{i,GDC}$, $\sigma_{e,GDC}$, and $\sigma_{e,Ni}$ are the intrinsic ionic or electronic conductivities of dense GDC and Ni. The factors ε_{GDC} and ε_{Ni} correspond to the volume fraction of each phase, while τ_{GDC} and τ_{Ni} are the tortuosities describing the elongation of the transport pathways.

In this work, different cells exhibited varying degrees of Ni percolation. The cell prepared by infiltrating GDC into a Ni skeleton showed excellent Ni percolation, meaning that most of the electronic conduction occurs along the Ni network. Therefore, in the TLM, the resistance of the electronic path can be set to 0. In contrast, all other electrode types exhibited poor Ni percolation, indicating that electronic conduction occurs mainly via the GDC phase. Consequently, its electronic conductivity must be taken into account. Under reducing operating conditions, the

electronic conductivity decreases strongly with increasing p_{O_2} , but remains much higher than the ionic conductivity (Figure 2.2(b)). Thus, charge transport is limited by ionic transport in GDC.

An exemplary impedance of the TLM and the corresponding DRT are shown in Figure 2.8(b, c). The Nyquist plot exhibits roughly two arcs, with the low-frequency arc dominating the overall impedance. The corresponding DRT in Figure 2.8(c) reveals a series of decaying peaks. Notably, four peaks are observed, although only three processes (charge transfer, ionic transport, and electronic transport) are considered. A systematic but qualitative investigation of the impact of charge-transfer resistance, charge carrier transport, layer thickness, and multilayer structures on impedances and DRTs is conducted based on the TLM using MATLAB® Simulink and presented in Appendix A.1. To reduce computational effort, the unit layer was assumed homogeneous, with $n = 1$ in the RQ element representing the charge-transfer process.

2.9 Distribution of Relaxation Times Analysis and Equivalent Circuit Fitting

2.9.1 Distribution of Relaxation Times

Impedance spectra are commonly evaluated using ECMs composed of the elements introduced in the previous sections. However, constructing an ECM for a given electrochemical system is challenging (223, 219):

1. Prior knowledge of the system is required, which may not be available.
2. Multiple circuit configurations can yield identical overall impedance, leading to non-uniqueness.

An alternative approach is the Distribution of Relaxation Times (DRT), which does not require a predefined ECM. Any capacitive system can be roughly described by a series connection of RC elements with an additional resistance (240). The resistance distribution of the RC elements over their associated time constants $\tau = R \cdot C$ gives the DRT function, transforming the impedance spectrum into the frequency domain without prior assumptions (241, 223).

The concept of relaxation times was introduced by Schweidler in 1907 (242) and expanded by Wagner in 1913 to a sum of relaxation times (243). Schichlein (241, 223) developed a methodology for directly calculating the DRT from measured SOFC impedance spectra. The DRT enables identification of individual loss processes with significantly higher frequency resolution compared to the Nyquist plot (236, 244, 80, 219, 245, 59).

The impedance can be expressed in terms of the distribution of relaxation times (DRT) as:

$$Z(\omega) = R_{\text{Ohm}} + \int_0^\infty \frac{g(\tau)}{1 + j\omega\tau} d\tau, \quad (2.74)$$

where R_{Ohm} is the ohmic resistance and $g(\tau)$ is the DRT function. In this formulation, $g(\tau)$ already contains the polarization resistance, i.e., its integral corresponds to R_{Pol} :

$$\int_0^\infty g(\tau) d\tau = R_{\text{Pol}}.$$

For practical evaluation, the integral is approximated by a discrete sum of N RC elements with logarithmically distributed relaxation times τ_n :

$$Z(\omega) = R_{\text{Ohm}} + \sum_{n=1}^N \frac{g_n}{1 + j\omega\tau_n}, \quad (2.75)$$

where g_n represents the contribution of the n -th RC element to the total polarization. Solving for g_n requires the inversion of an integral or summation equation, the solution of which is a mathematically ill-posed problem (246, 241). Therefore, the inverse problem is solved numerically and stabilized using Tikhonov regularization (247).

To distinguish the numerically approximated distribution function from the analytically determined one, they are often denoted as $g(\tau)$ or $g(f)$ in the literature (241, 223, 219). The regularization introduces a smoothing of the distribution, controlled by the parameter λ_{DRT} . The optimal value of λ_{DRT} is determined empirically for the considered electrochemical system and measurement setup. It should be chosen (i) large enough to suppress artifacts and measurement noise, but (ii) sufficiently small to avoid excessive loss of spectral resolution due to over-smoothing.

At IAM-ET, the DRT calculation is implemented in the All-Fit program using MATLAB®. The DRT is visualized with $g(f)$, serving as a measure of the impedance contribution. It is plotted as a function of the frequency f , as shown in Figure 2.9.

In the case of ideal processes, which can be described by RC elements, the DRT calculation results in Dirac impulses $\delta(f - f_n)$ at the corresponding frequencies, as shown in Figure 2.9(a). However, in real systems, a distribution of reaction zones leads to an expansion of relaxation times around a characteristic frequency (Figure 2.9(b)). The area enveloped within a peak represents the resistance value for the corresponding process. The number of peaks in the DRT provides an initial indication of the total number of ongoing processes, while the peak frequency indicates

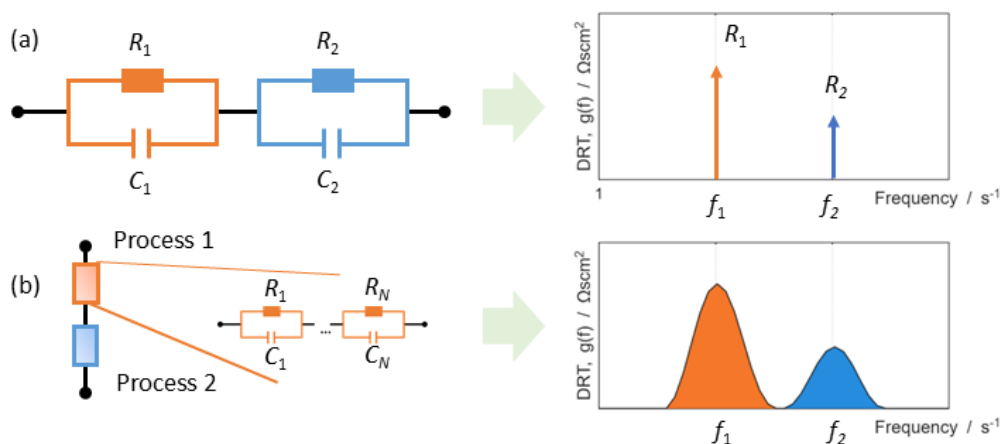


Figure 2.9: Calculated DRTs based on: (a) an equivalent circuit consisting of two ideal processes (RC elements), (b) an equivalent circuit consisting of two real processes (RQ elements). The orange and blue areas equal the resistance of processes 1 and 2.

the speed of the processes. The shape of the peaks can provide information about the origin of the processes. However, the superposition of multiple processes cannot be ruled out. Therefore, a sensitivity analysis is required to clearly identify peaks to specific physicochemical processes, as illustrated in Section 4.3.

2.9.2 Complex Non-Linear Least Squares (CNLS) Fit

By combining the DRT with a sensitivity analysis, it is possible to establish a physically motivated ECM for the investigated system based on the dependencies of the individual processes (80). The ECM is evaluated using the CNLS fitting procedure, in which the model parameters of the ECM elements are iteratively optimized.

The fitting procedure involves:

1. Selection of a suitable ECM,
2. Initialization of model parameters using DRT information,
3. Iterative CNLS fitting to minimize quality criterion S ,
4. Validation of fit quality based on residual errors and consistency.

The CNLS procedure seeks the parameter set

$$\vec{x} = (x_1, x_2, x_3, \dots)$$

that minimizes the deviation between measured and simulated complex impedance spectra.

The quality criterion S used in this work is defined as (219):

$$S = \sum_{m=1}^M [w_{Z'} r_{Z',m}^2 + w_{Z''} r_{Z'',m}^2 + w_{\text{DRT}} r_{\text{DRT},m}^2] \rightarrow \min \quad (2.76)$$

with weighting factors w_i and the corresponding squared residuals r_i^2 . Including the DRT error as an additional criterion significantly reduces the influence of measurement artifacts on the fit results (219). The residuals r_i are evaluated at each measured or simulated frequency value ω_m and normalized to the amplitude of the measured quantity i (219, 248):

$$r_{Z',m} = \frac{Z'_{\text{meas}}(\omega_m) - Z'_{\text{mod}}(\omega_m, \vec{x})}{|Z_{\text{meas}}(\omega_m)|}, \quad (2.77)$$

$$r_{Z'',m} = \frac{Z''_{\text{meas}}(\omega_m) - Z''_{\text{mod}}(\omega_m, \vec{x})}{|Z_{\text{meas}}(\omega_m)|}, \quad (2.78)$$

$$r_{\text{DRT},m} = \frac{\gamma_{\text{meas}}(\omega_m) - \gamma_{\text{mod}}(\omega_m, \vec{x})}{|\gamma_{\text{meas}}(\omega_m)|}. \quad (2.79)$$

The MATLAB[®] `fmincon` function is employed for optimization. In this work, a weighting scheme of $Z' : Z'' : \text{DRT} = 2 : 1 : 1$ is applied, thereby prioritizing the real part of the impedance and the DRT contribution. An oscillatory distribution of r_i around zero indicates a good fit, whereas systematic drifts indicate model inadequacies or poor initialization of parameters.

3 Experimental

In this chapter, the technical implementation of the conducted experiments is described. This includes: (i) a detailed introduction of the investigated cells and (ii) their manufacturing process, (iii) an introduction to the novel active-driven gas layer concept and measurement setup, (iv) characterization methods and operation procedures used for the investigation of the pseudo-inductive phenomenon, sensitivity test, and degradation, (v) an evaluation of the quality of impedance data via the Kramers–Kronig (KK) validity test and (vi) a brief introduction of the post-test analysis techniques, including EDS, SEM, STEM, and FIB-SEM.

In this study, the cell ID is defined as a composite label combining the test number and the cell variant (e.g., IS1-446_V1.2b). When multiple cells of the same variant were tested in a single assembly, the cell ID is given as IS1-xxx_Vx.x_n, where n indicates the nth cell of variant Vx.x, numbered from the top of the assembly in test IS1-xxx.

3.1 Cell Structure

This work focuses on the characterization and degradation analysis of various electrolyte-supported symmetrical cells with Ni/GDC anodes. The cells were produced at Forschungszentrum Jülich GmbH, with electrodes fabricated via screen printing and infiltration on commercial 8YSZ electrolyte substrates (200 μm , Kerafol GmbH & Co. KG, Eschenbach i. d. Opf., Germany).

To target intermediate operating temperatures ($< 600\text{ }^{\circ}\text{C}$) and investigate aging behavior, several cell variants were fabricated, differing in layer sequence, fabrication techniques, paste composition, and sintering temperature. Figure 3.1 schematically presents the configurations of the experimental cells with and without a GDC interlayer. Compared to the 200 μm -thick electrolyte, all other layers are relatively thin: the GDC interlayer is approximately 4 μm , the Ni/GDC layer ranges from 8–20 μm depending on the cell type and the Ni current collector varies between 4–8 μm depending on Ni/NiO particle size used in the paste. The electrically active area of each electrode is 1 cm^2 with a GDC interlayer slightly larger underneath ($1.2 \times 1.2\text{ cm}^2$). Layer thicknesses after reduction were measured using SEM, as illustrated in Figure 3.1(c) for symmetrical cells IS1-444_V1.2 (with GDC interlayer) and IS1-454_V1.2b (without interlayer), for example.

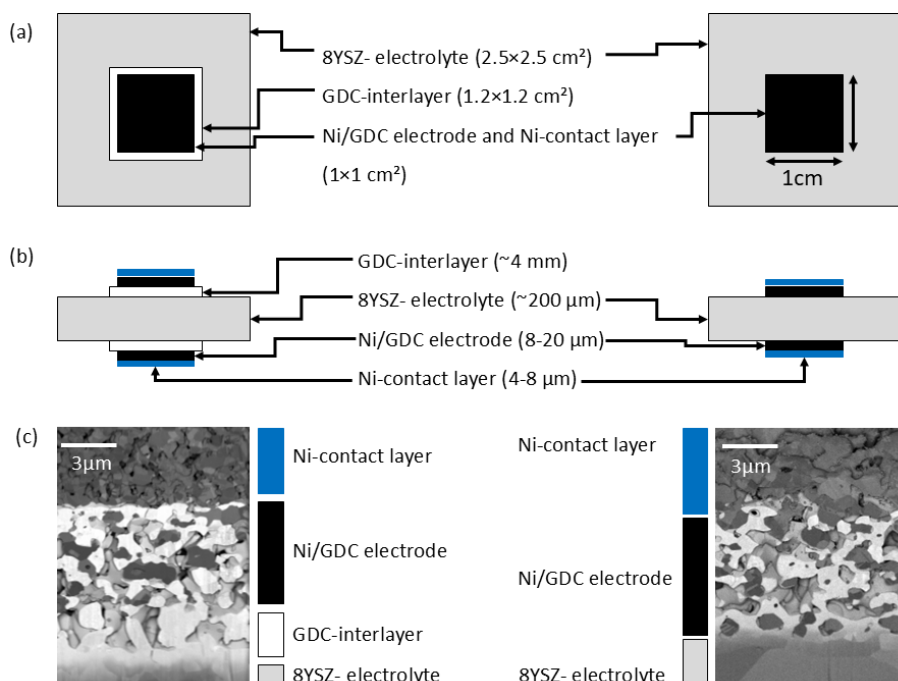


Figure 3.1: (a, b) Schematic configurations (top and side view) of the experimental cells and (c) cross-sectional SEM/BSE images of cells IS1-444_V1.2 and IS1-454_V1.2b. In the area of Ni/GDC electrodes, the lighter gray denotes GDC, and the darker gray Ni. Note that Figure (b) is not to scale. Adapted from (7).

3.2 Cell Production Procedure

State-of-the-art Ni/GDC fuel electrodes produced via screen printing are optimized for electrolyte-supported cells operating at 750°C to 900°C . Their coarse microstructure ensures sufficient performance at higher temperatures while guaranteeing excellent durability under such conditions. But they exhibit limited performance at 600°C (polarization resistance of approximately $0.800 \Omega \text{ cm}^2$) (86).

One of the objectives is the development of Ni/GDC fuel electrodes suitable for low-temperature operation ($< 600^\circ\text{C}$) that exhibit excellent initial performance and high resistance to degradation. Several attempts were made to enhance anode performance, including variations in sintering temperatures for screen-printed layers, the use of nanoscale particles in slurry, and the infiltration of fine particles into screen-printed skeletons. In total, seven different cell variants were fabricated. An overview of the fabrication workflows is presented in Figure 3.2. Detailed descriptions of all fabrication parameters are provided in Appendix A.2.

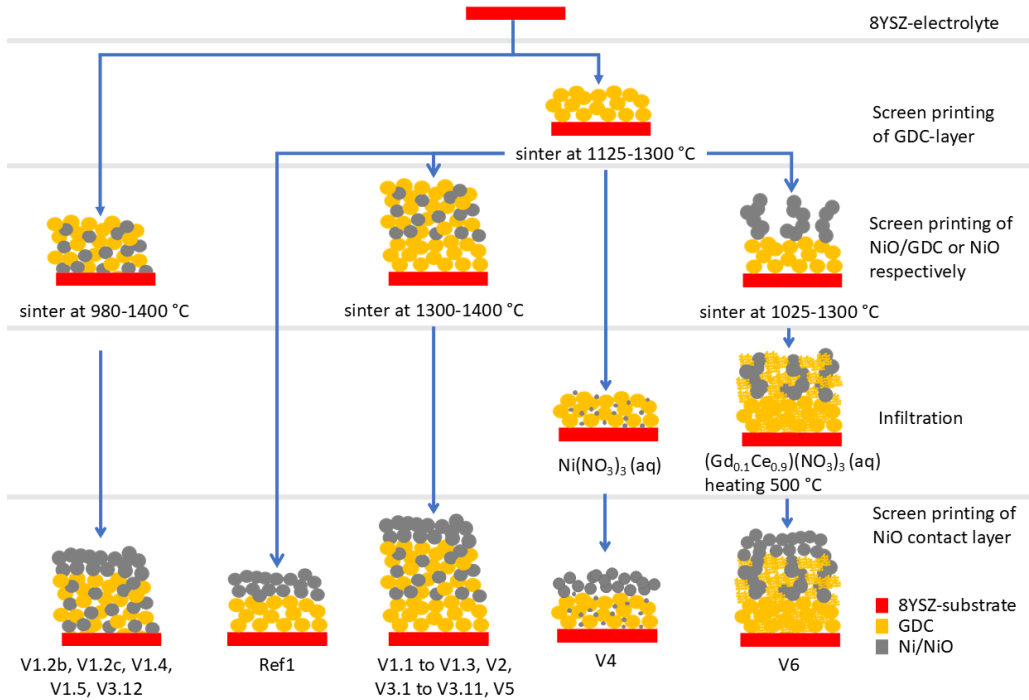


Figure 3.2: Schematic illustration of manufacturing steps for the seven electrode variants. All cells are symmetrical. Thus, only one electrode is shown. Adapted from (6). A more detailed description of the fabrication is shown in A.2.

Cell variants Ref1, V1–V3, and V5 were produced via sequential screen printing of different layers, while V4 and V6 involved screen printing followed by infiltration. The GDC powder ($\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$) was first transformed into a paste. For this purpose, α -terpineol was used as a dispersion medium and ethylcellulose as a binder. As shown in Figure 3.2, starting from an 8YSZ substrate (200 μm), a GDC paste was screen-printed and sintered at 1300 °C. Based on this interlayer, cell type Ref1 was obtained by screen-printing a NiO layer with a particle size of 0.5 μm . Similarly, NiO/GDC pastes were screen-printed and sintered at 1300–1400 °C to produce cell variants V1.1, V1.2, V1.3, V2, V3.1 to V3.11, and V5, using GDC and NiO powders in a 50:50 wt% ratio.

The paste used for V1 and V2 was originally developed for anode-supported cells targeting operation at 800 °C. Therefore, the sintering temperature was increased to ensure sufficient densification of the electrolyte. After initial characterization and obtaining a first impression of the aging behavior of these cells, it was decided that cells without an interlayer were suitable for durability testing and modeling.

Thus, several sub-variants of V1 and V3 were produced by skipping the screen-printing step for the interlayer. Starting from an 8YSZ electrolyte, NiO/GDC paste was directly screen-printed onto the substrate and sintered at 980–1400 °C. Subsequently, a NiO ($d_{\text{NiO}} = 0.5 \mu\text{m}$) or Ni ($d_{\text{Ni}} = 1.4 \mu\text{m}$) layer was screen-printed on top of the electrode, yielding the sub-variants V1.2b/c, V1.4a/b, V1.5a/b, and V3.12a/b/c.

Variant V4 started from a YSZ substrate with a sintered GDC interlayer, which was infiltrated with a 3 mol/L $\text{Ni}(\text{NO}_3)_2$ solution and dried at 90 °C overnight. The infiltration was repeated several times (1-3) to achieve varying Ni loadings. Finally, the NiO ($d_{\text{NiO}} = 0.5 \mu\text{m}$) layer was printed atop the Ni-infiltrated GDC layer.

For variant V6, a NiO paste was first screen printed onto the GDC interlayer and sintered at 1025-1300 °C to form the NiO backbone. The cells were then immersed in a $(\text{Gd}_{0.1}\text{Ce}_{0.9})(\text{NO}_3)_3$ solution for 5 min, dried overnight at 90 °C and calcined at 500 °C. This step was repeated multiple times (5-15) to ensure sufficient GDC content. Finally, the NiO ($d_{\text{NiO}} = 0.5 \mu\text{m}$) layer was printed on top. Two concentrations were used, one at 3 mol/L and the other supersaturated.

Figure 3.3 shows SEM images of exemplary cells from variants Ref1, V1, V4, and V6 after reduction at 650 °C in the BSE mode. Cell variants Ref1, V1, and V4 possess GDC interlayers of $\sim 4.8 \mu\text{m}$ thickness, while cell variant V6 has nearly double the thickness. Variants V2, V3, and V5 are not included, as they share the same layer sequence and GDC interlayer thickness as variant V1, differing only in the composition of the Ni/GDC layer. The V1 subvariants without a GDC interlayer are also omitted because their layer sequence is equivalent to that of the V4 variants. Due to incomplete sintering, the Ni contact layer occasionally exhibited poor adhesion and delamination during cell removal.

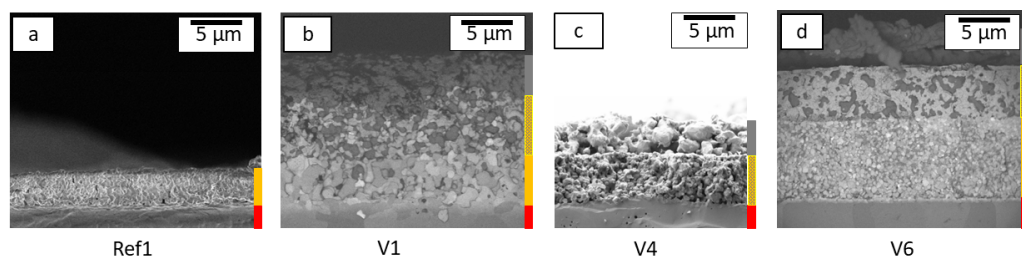


Figure 3.3: SEM images of electrodes from cells (a) IS1-442_Ref1, (b) IS1-442_V1.2, (c) IS1-462_V4.5b, (d) IS1-438_V6.5 after reduction and short-term testing at 600°C. Electrolyte substrate is depicted in red, GDC layer in orange, Ni contact layer in gray, Ni/GDC layer in orange with gray meshes. Darker gray in the Ni/GDC layer corresponds to Ni, and lighter gray corresponds to GDC. Adapted and modified from (6). Figures (a, b, d) were recorded in BSE mode with a tilt angle of 54°, while Figure (c) was recorded using in-lens mode.

3.3 Test Setup Introduction

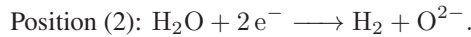
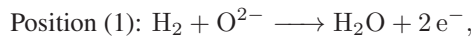
3.3.1 Active Driven Gas Layer

In this dissertation, predicting electrode lifetimes requires a large number of tests and long test durations. Efforts have been made to reduce both while ensuring the reliability of the obtained results. Simultaneous testing of multiple cells in a single setup improves statistics and enables direct comparison of different cell variants.

One approach involves using a rainbow stack (249), which allows simultaneous testing of many cells but requires expensive stack production and carries the risk that a broken cell may accelerate aging in the other cells. Alternatively, multiple cells can be tested in a single chamber with an appropriate sample holder. As a single gas composition is applied to all electrodes, this approach is limited to symmetrical cells. An innovative method coupling electrochemical and microstructural life testing was presented in (250), involving current-switching operations on six parallel-connected symmetrical SOCs. To analyze microstructural changes over time, cells were removed sequentially from the test bench. However, the silver paint current collector negatively affected electrode durability.

For a similar purpose, we developed a test method that enables simultaneous testing of multiple symmetric cells in a single reducing-gas atmosphere. This method minimizes the contributions of polarization associated with gas conversion and diffusion by employing the concept of an active-driven gas layer (251). The ceramic sample holder, presented in Figure 3.4(a), allows assembling of multiple cells. Between the cells, highly porous Ni meshes are interposed and connected by Pt wires. This arrangement enables voltage and impedance measurements on each cell in the assembly using a multiplexer.

The configuration of the test setup is depicted in Figure 3.4(b) (note: not to scale). In one symmetrical cell, the electrode positions are labeled as:



The fuel is consumed at position (1) and generated at the electrode of the next cell (position (2)) across the Ni mesh. This guarantees strictly perpendicular gas transport, independent of flow rate and flow field geometry. The top and bottom cells are excluded from testing due to their asymmetric gas-transport properties. For fixation, contacting, and sealing, no glass sealant, ceramic glue, or silver paint is used. Instead, cells are contacted using nickel or gold meshes,

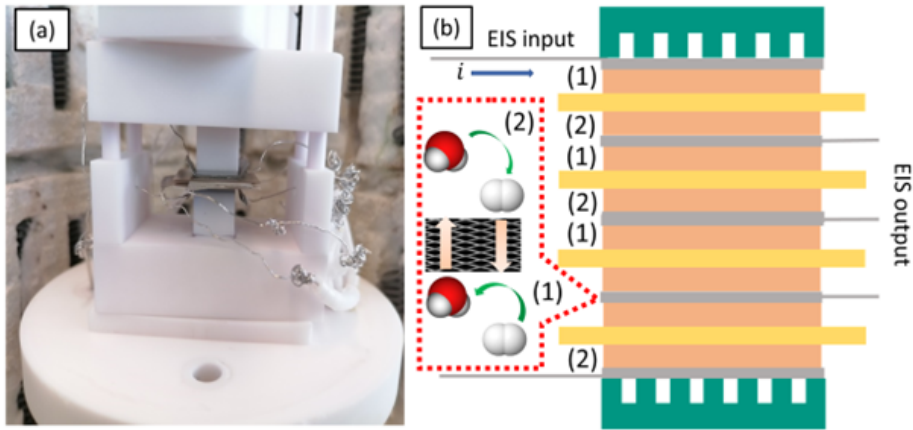


Figure 3.4: (a) Photograph of the sample holder with weights placed on top and integrated cells. (b) Schematic representation of the multi-cell test setup implementing the active-driven gas layer concept. The ceramic flow field is shown in green, the current collector, associated nickel meshes and wires in gray, the 8 mol% YSZ electrolytes in yellow, and the electrodes (including the GDC interlayer) in orange. In the red dialog box, red and white balls represent oxygen and hydrogen atoms, respectively. Light red arrows indicate the direction of gas transport for hydrogen and steam, while the blue arrow denotes the assumed current flow direction. Figure obtained from (5).

which are held in place by weights on top of the sample holder. This modification provides greater flexibility for cells of various sizes and shapes.

To further reduce contact resistance, the contacts are additionally weighted with approximately 200 g of ceramic blocks.

3.3.2 Measurement Setup

As shown in Figure 3.5(a), the 4-cell assembly in the ceramic holder is connected to a Solartron 1260 frequency response analyzer (FRA) (252), which allows measurement of the complex internal resistance over a frequency range from 10 mHz to 1 MHz. To minimize parasitic effects on the impedance measurement, the current- and voltage-carrying leads are spatially separated, twisted, and magnetically insulated by Al_2O_3 . The top and bottom Ni meshes are connected to the excitation signal from the FRA, which is controlled by a measurement script to induce a voltage response ≤ 12 mV on each cell. Response signals are collected from the three Ni meshes between the cells. A multiplexer allows automatic characterization of multiple cells. The frequency range is $0.03 \text{ Hz} \leq f \leq 1 \text{ MHz}$. Measurements were performed under open-circuit (no-load) conditions.

In practice, the Pt wires connected to the Ni meshes are routed to a 10-pin pluggable terminal block on the voltage switch box. Two pins are reserved for the lambda sensor, leaving eight pins

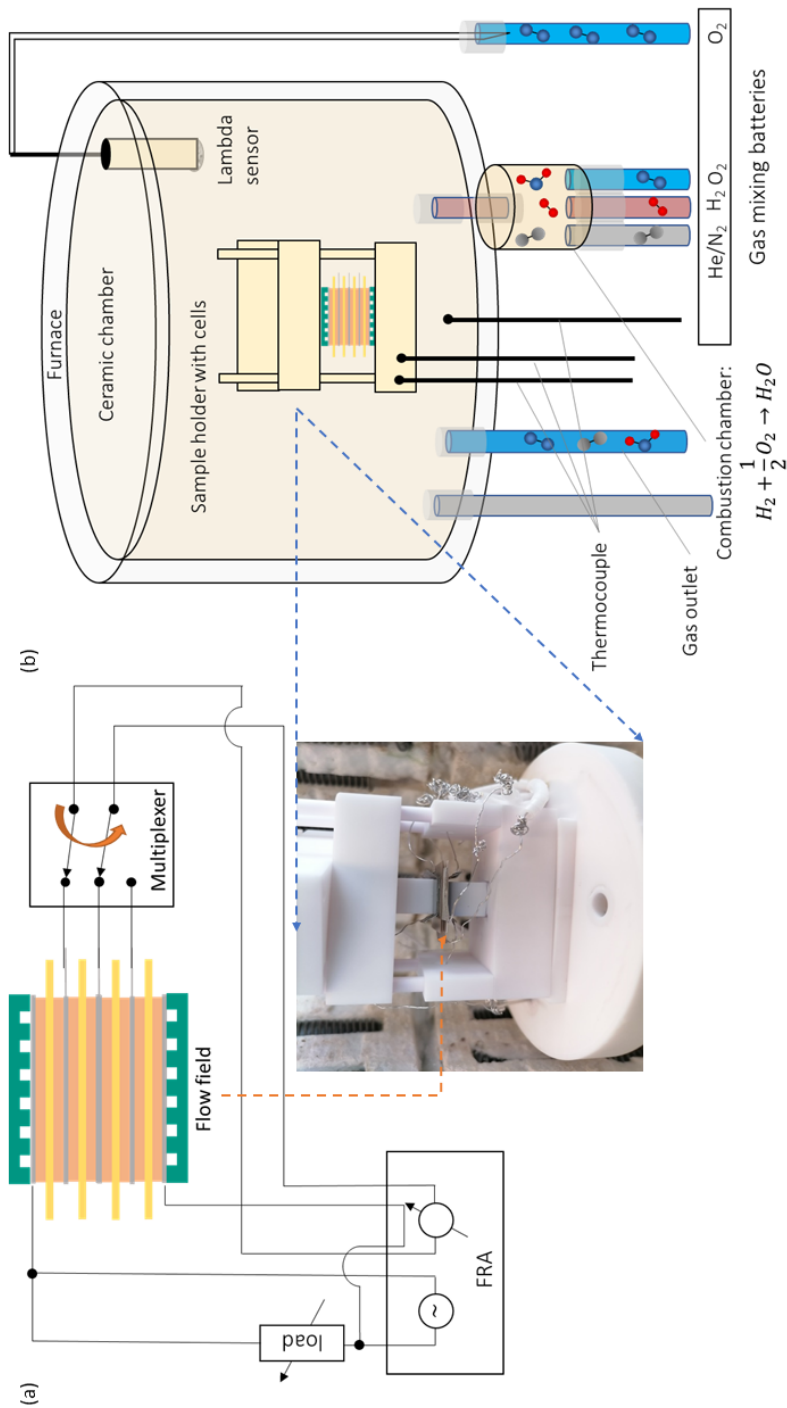


Figure 3.5: (a) Schematic of electrochemical test setup for multi-cell impedance characterization. (b) IS1 measurement setup with furnace, gas supply, ceramic sample holder in (a) is obtained from (4) and is also shown in Figure 3.4.

available for voltage scanning. The voltage of an individual cell is obtained from the potential difference between two adjacent Ni meshes, corresponding to two adjacent pins on the terminal block. Consequently, eight pins allow the simultaneous measurement of up to seven cells. The multiplexer can switch among up to 7 channels.

Electrochemical characterization of the cells (Figure 3.1) in the sample holder (Figure 3.4(a)) was conducted using the IS1 measurement setup (Figure 3.5(b)). The setup is integrated into an electrically heated furnace, allowing precise control of cell temperature up to 1000 °C. Type S thermocouples (Pt and Pt-10% Rh) are placed near the sample holder for temperature monitoring. A lambda sensor monitors the humidity inside the chamber and detects potential leaks.

Gas supply is controlled by an internal gas mixing unit that allows precise control of variable gas mixtures via solenoid valves and mass flow controllers (MFC). Fuel gas humidification is achieved by Pt-catalyzed combustion of H₂ with O₂ in an Al₂O₃ chamber, offering high accuracy compared to conventional bubbler systems. Inert gases (N₂ and He) are supplied for investigating diffusion losses. Gas diffusion effects were isolated by substituting the inert gas component in otherwise identical ternary gas mixtures and comparing the resulting polarization resistances. A detailed introduction can be found in (86). All tests use a total volumetric flow rate of 500 mLmin⁻¹ under atmospheric conditions. To monitor humidity in the test chamber, a stable volumetric flow rate of 50 mLmin⁻¹ of air is supplied to one side of the lambda sensor.

The measurement station and peripherals are controlled via AKSOFC software, which enables script-based control of gas mixing, the electronic load, and the FRA, as well as automated monitoring of voltages, current densities, gas flows, and temperatures. All experiments in this work were conducted at the IS1 measurement station. Detailed descriptions of single-cell setups, which are identical to IS1 except for the structure in the furnace, are provided in (253, 254, 218).

3.4 Validation of Novel Test Method

The testing of symmetrical cells in a stack-like arrangement with active-driven gas layers (Figure 3.4) in principle supports:

1. Increasing statistics and enabling microstructural investigation of samples removed after defined periods during long-term tests.
2. Testing the performance and durability of different electrodes/cells simultaneously.

The validation of this approach employs four sub-variants from the V1 group (V1.2, V1.4a, V1.5a, V1.2b) and one cell from V4.6, as summarized in Table A.7.

Test 1: Identical cells Three cells from the same batch of variant V1.2 were assembled, with two additional V1.2 cells placed at the top and bottom (Figure 3.6(a)). The cells were heated in N_2 to 800 °C, reduced in N_2/H_2 for 1 h, and subsequently adjusted to a 50:50 H_2/H_2O atmosphere by introducing an O_2 flow of 0.125 mLmin^{-1} . Initial EIS measurements were conducted at 800, 650, and 600 °C. The cells were then heated to 900 °C and measured continuously. This test sequence was repeated three times, providing data for the pristine state as well as durability tests of 250 h and 1,100 h. The corresponding results are discussed in Section 4.4.1.1.

Test 2: Different cells Three cells from variants V1.4a, V1.5a, and V1.2b were assembled with two cells from variant V1.2 at the top and bottom (Figure 3.6(b)). Mid-term aging at 700 °C for 900 h was conducted after reduction and initial characterization, followed by EIS under varied operating conditions, including gas composition and inert gas type. During these tests, an inductive loop was observed in the impedance spectra of the cell in the center. To investigate its origin, a comparative test series was conducted, examining the impedance response of a cell under both multi-cell and single-cell configurations.

Test 3: Comparison to single-cell setup Cell from V4.6 was first tested in a single-cell setup at 600 °C (Figure 3.6(c)), then sandwiched between two cells from V1.2 in a multi-cell assembly (Figure 3.6(d)) under identical conditions.

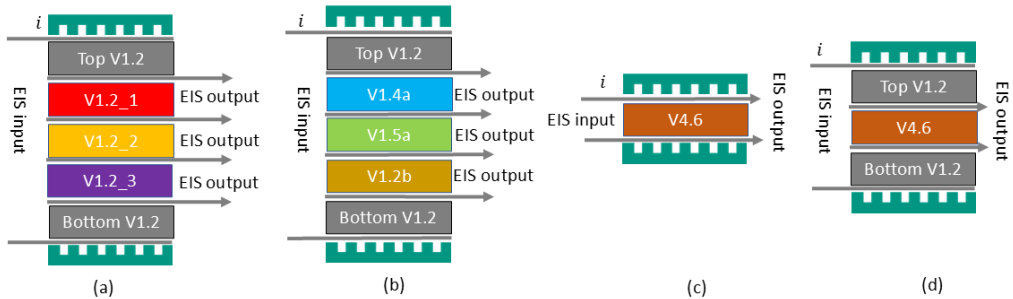


Figure 3.6: Schematic of validation tests: (a) identical cells, (b) different cells, (c) a cell in a single-cell setup, and (d) in a multi-cell setup. Adapted from (5).

The results of Test 2 and 3 are illustrated in Section 4.1.

3.5 Cell Test Protocols

As the focus of this work is the characterization and degradation prediction, the symmetrical ESCs were operated exclusively under a reducing atmosphere (hydrogen, water vapor, and inert gas) and measured under OCV conditions. The test procedure consists of three phases:

1. **Reduction Procedure:** Heating, reduction and initial characterization.
2. **Measurement Phase:** Characterization, accelerated durability, and sensitivity testing.
3. **Cool Down Phase:** Controlled cooling in a reducing atmosphere.

3.5.1 Reduction Procedure

To investigate the influence of the reducing temperature, three different reduction routines were carried out:

1. **Standard FZJ reducing protocol:** Cells are heated to 800 °C in N₂ (95%)/H₂ (5%) at 3 K min⁻¹. After adjusting the gas composition to H₂ (0.5 L min⁻¹) and O₂ (0.125 L min⁻¹) to produce a 1:1 H₂/H₂O mixture in an upstream burner, cells are characterized using EIS at 800, 650, and 600 °C.
2. **Intermediate reducing protocol:** Cells are gradually heated in N₂ (95%)/H₂ (5%) at 1 K min⁻¹ until 650 °C. Gas composition is then changed to N₂ (65%): H₂ (30%): H₂O (5%) and maintained for 6 h. After adjusting to H₂ (0.50 L min⁻¹) and O₂ (0.125 L min⁻¹) to form a 1:1 H₂/H₂O mixture, cells are characterized at 650 and 600 °C.
3. **Extra-fine reducing protocol:** For cells with fine Ni structure (variants V3 and V4), a reduced temperature protocol is applied. Cells are gradually heated in N₂ (95%)/H₂ (5%) at 1 K min⁻¹ until 550 °C. Gas composition is then changed to N₂ (65%): H₂ (30%): H₂O (5%) and maintained for 6 h. After adjusting to H₂ (0.50 L min⁻¹) and O₂ (0.125 L min⁻¹), cells are characterized at 550 and 500 °C.

Some of the cells that underwent only the reduction procedure are listed in Table A.8.

3.5.2 Measurement Phase

After reduction and initial characterization, the performance was first evaluated through reference measurements at nominal operating points (600 °C with a 1:1 H₂/H₂O mixture). Cells with

polarization resistance $> 0.800 \Omega\text{cm}^2$, inadequate mechanical stability, or low reproducibility were excluded from further testing. Subsequently, extensive variation in fuel-gas humidity or hydrogen partial pressure (5–50 %) and temperature (600–900 °C) was applied to enable unambiguous process identification. The gas diffusion losses were investigated by alternating the inert gas between helium and nitrogen. This sensitivity test procedure is analogous to that reported in (196) and therefore not described in further detail here. The cells that underwent this procedure are listed in Table A.9.

To design the accelerated stress test protocol, cells with moderate initial performance and reliable mechanical stability were tested at different temperatures (600–900 °C) and varying humidities (10–50 %) for up to 1,100 h. Based on the results, the cell variants suitable for further modeling and the appropriate stressor range were determined. The initial durability tests were performed under the conditions listed in Table 3.1. The corresponding tests and cell variants (cell IDs) are listed in Table A.10.

Table 3.1: Test conditions at elevated temperatures with varying humidity for the first impression of aging behavior.

Temperature / °C	Steam partial pressure / bar	Hydrogen partial pressure / bar
900	0.5	0.5
800	0.5	0.5
800	0.1	0.9
750	0.5	0.5
700	0.5	0.5
600	0.5	0.5

Afterwards, accelerated stress tests were conducted on the selected cell variant V1.5a. Cells were operated under elevated-stress conditions (600–750 °C, 10–50 % humidity) for varying durations. The test conditions were summarized in Table 3.2. The corresponding tests and cell IDs are listed in Table A.11.

Reference impedance measurements at 600 °C under 50% humidified hydrogen were performed intermittently at varying intervals. During the first 240 h, reference measurements were conducted more frequently, approximately every 80 h. Between 240 and 640 h, the interval was increased to about 100 h, then extended to approximately 200 h. Consequently, for a total test duration of 1000 h, up to ten reference measurements were typically obtained.

The cells were cooled from the elevated test temperature to 600 °C at a rate of -3 K/min. Once the target temperature was reached, the gas atmosphere was adjusted to the nominal conditions. The cells were then held under these conditions for 1 h to allow equilibration of the oxygen

Table 3.2: Accelerated stress test conditions for aging modeling.

Temperature / °C	Partial pressure		Test duration / h
	Steam ($p_{\text{H}_2\text{O}}$) / bar	Hydrogen (p_{H_2}) / bar	
750	0.5	0.5	450
725	0.5	0.5	480
700	0.5	0.5	550
650	0.5	0.5	590
625	0.5	0.5	2700
600	0.5	0.5	1000
600	0.5	0.5	0
600	0.3	0.7	800
600	0.1	0.9	1000

stoichiometry in GDC. After completion of the EIS measurement, the cells were reheated to the original test temperature at 3 K/min and maintained at that temperature for an additional 1 h to re-establish thermodynamic equilibrium, following atmospheric adjustment, before resuming the aging test. Depending on the temperature and atmosphere differences, one complete reference measurement procedure required approximately 6–10 h.

3.5.3 Cool Down Phase

At the end, cells were cooled to room temperature under controlled conditions to prevent Ni reoxidation, which would irreversibly alter microstructure and cause anode expansion (255).

The chamber was flushed with 100% H_2 to remove oxygen for 10 min. Cooling was carried out under a protective $\text{H}_2:\text{N}_2$ environment with a ratio of 1:1 until 400 °C, then 1:4 from 400 °C to room temperature at a rate of -3 K/min.

3.6 Measurement Data Quality

The consistency and quality of the recorded impedance spectra are crucial for meaningful analysis of the measurement data using DRT and equivalent circuit models. The calculation of the impedance from the excitation and response signals is only valid if the assumptions of causality,

linearity, and time invariance are fulfilled. To obtain error-free, high-quality impedance spectra across the entire frequency range, a high signal-to-noise ratio (SNR) is required.

An established method for assessing consistency and quality is the Kramers–Kronig validity test (221, 222, 93, 220). This method verifies the Kramers–Kronig relations, which relate the real and imaginary parts of an impedance spectrum. The Kramers–Kronig relation is based on frequency-domain transformations, first introduced in 1926 by Kronig (256) and in 1929 by Kramers (257).

If the above-mentioned assumptions are satisfied, the real part can be calculated from the imaginary part and vice versa, using integral equations. The validity of this relation is verified based on the procedure described in (221, 220). The applicability of the relation is quantitatively assessed using the Kramers–Kronig residuals, which describe the deviation between the calculated and the measured real or imaginary parts.

3.7 Post-Test Analysis

After electrochemical characterization and durability testing, selected samples were fractured for subsequent structural analysis. The electrode composition, as well as interdiffusion phenomena and interface formation, were investigated using Energy-Dispersive X-ray Spectroscopy (EDS). The microstructural properties of the porous electrodes were analyzed by SEM, STEM, and destructive FIB/SEM tomography. The last technique combines SEM imaging with successive material removal by a Focused Ion Beam (FIB), enabling three-dimensional reconstruction of the electrode. The FIB/SEM measurements and subsequent segmentation were performed by Dr. Ardavan Makvandi at the Laboratory for Electron Microscopy (LEM, KIT) and Dr. Matthias Wieler at Bosch, Renningen. An overview of the applied imaging techniques and the associated preparation steps for FIB-SEM is provided below.

3.7.1 Energy-Dispersive X-ray Spectroscopy (EDS)

Energy Dispersive X-ray Spectroscopy (EDS, also referred to as EDX or EDXS) is a widely used technique for material characterization in electron microscopy. In EDS, X-rays are generated when primary electrons interact with atoms in the sample. Inner-shell electrons can be activated, and when outer-shell electrons fill these vacancies, characteristic X-rays are emitted. The efficiency of this process, known as the fluorescence yield, increases with atomic number, making the detection of light elements more challenging (258, 259, 260).

Modern detectors, particularly silicon drift detectors, provide high sensitivity and rapid acquisition, enabling analysis of both solid and biological samples. SEM-based EDS benefits from low acceleration voltages, which reduce the interaction volume and improve surface sensitivity. The detector converts X-ray energy into voltage pulses, which are digitized and processed to produce a spectrum displaying characteristic peaks overlapped on a continuous bremsstrahlung background (261).

The key parameters influencing the quality of EDS data include beam energy, overvoltage, detector type, and acquisition time. Proper selection of these parameters ensures high spectral resolution while maintaining the detector's dead time within recommended limits (typically 15–50%). When combined with SEM imaging, EDS provides spatially resolved chemical analysis, offering information on the composition of microstructural features, phases, or inclusions (261).

In this study, EDS was used to determine the elemental composition of the samples. Measurements were performed in combination with SEM using an XFlash Detector 5030 (Bruker AXS, Karlsruhe, Germany).

3.7.2 Scanning Electron Microscopy (SEM)

In an electron microscope, electrons are used for imaging instead of light. The achievable resolution d_{res} is fundamentally limited by the wavelength λ according to the Abbe equation. While visible light ($\lambda \approx 400$ nm) yields a resolution of about 200 nm, the much shorter electron wavelength (3–12 pm) enables resolutions down to 0.1 nm. Compared to optical microscopy, electron microscopy additionally offers greater depth of focus, a wider range of contrast mechanisms, and more straightforward image interpretation (262).

A scanning electron microscope generates a primary electron beam (1–40 keV), which is focused to a sub-10 nm probe and raster-scanned across the specimen. Beam-sample interactions produce secondary electrons (SE), backscattered electrons (BSE), and X-rays. SE are low-energy electrons (<50 eV) that escape only from near-surface regions and are therefore highly surface-sensitive, whereas BSE originate from deeper elastic collisions and provide compositional contrast depending on atomic number. Consequently, SE imaging primarily reveals surface topography, while BSE imaging emphasizes material contrast (262).

The quality of SEM images depends on the number of detected electrons per pixel. Factors such as surface geometry (edge effect), charging, acceleration voltage, and specimen tilt strongly influence the SE signal. Noise from random fluctuations in signal generation can be reduced by increasing dwell time or averaging multiple scans. At low acceleration voltages (<5 kV), the

backscatter coefficient varies non-monotonically with atomic number, which can enhance contrast for specific material combinations (263, 264).

SEM images were primarily obtained with a ZEISS 1540 XB-SEM (Carl Zeiss NTS GmbH) in in-lens mode. For further details on SEM setup and operation at our institute, see (69, 59). To enhance contrast between Ni and GDC phases, imaging was performed in BSE mode using a Thermo Scientific™ Helios G4 FX DualBeam™ (Thermo Fisher Scientific, Waltham, MA, USA) at LEM, KIT.

3.7.3 Scanning Transmission Electron Microscopy (STEM)

STEM scans the sample with a focused electron probe, similar to SEM, but electrons penetrate through a thin specimen and are detected below the imaging lenses. Many TEMs can switch to STEM mode, while some dedicated STEM instruments cannot operate in conventional TEM mode. Typical operation voltages range from 60 keV to 300 keV. The most common detector is the radially segmented STEM detector, although angular segmented, pixelated, SE, X-ray, or energy-loss detectors are also used. This section covers spatial resolution, detectors, imaging modes, and nano-beam diffraction.

Spatial Resolution STEM resolution d_{reso} depends on the probe diameter d_{probe} , signal-to-noise ratio d_{SNR} , beam and sample stability d_{bb} and beam divergence d_{α} from the convergence angle (265, 266):

$$d_{\text{reso}} = \sqrt{d_{\text{probe}}^2 + d_{\text{SNR}}^2 + d_{\text{bb}}^2 + d_{\alpha}^2}. \quad (3.1)$$

Thicker specimens lead to greater broadening and divergence, whereas thin specimens can achieve atomic resolution. Unlike in TEM, magnification in STEM is controlled by the scan size rather than by the projection lenses (261).

STEM Detector and Image Formation The STEM detector is placed below the specimen and consists of a central bright-field (BF) segment and surrounding dark-field (ADF/HAADF) segments. Electron interactions generate electron-hole pairs separated in a biased semiconductor junction, producing a current

$$I_{\text{det}} = I_{\text{cc}} + I_{\text{b}}, \quad (3.2)$$

where I_{cc} is the collected signal and I_b is the dark current (267). Lenses between the specimen and detector adjust the detection-angle range, except in field-free STEM-in-SEM.

Image Contrast Bright-field segments collect the direct beam, while dark-field segments collect scattered electrons. HAADF intensity increases with thickness due to Rutherford scattering, providing Z-contrast for distinguishing materials of the same thickness. STEM images allow atomic-column resolution, and BF-STEM can reveal lattice fringes via phase contrast if diffraction discs overlap (261, 268).

Nanobeam Diffraction (NBED) NBED records diffracted intensities from nanometer-sized areas using a camera, rather than integrating them with a detector. It enables crystallographic analysis, structure identification, and strain measurements (269).

STEM combines SEM and TEM techniques. A focused electron beam scans the sample while transmitted electrons are detected, allowing analysis of internal structure at atomic resolution. Detectors capture elastically scattered electrons, providing information about the crystalline structure, and inelastically scattered electrons, revealing chemical composition. STEM analysis was performed on a single sample at LEM using the Thermo Scientific Helios G4 FX Nanolab. Sample preparation is partly the same as introduced in Section 3.7.4.1.

3.7.4 Three-dimensional Reconstruction

3.7.4.1 Sample Preparation

A major advantage of focused ion beam tomography is the strong contrast between different materials. Careful sample preparation is essential for obtaining accurate results and reducing effort during image processing. For this purpose, a segment of approximately $5 \times 5 \times 5 \text{ mm}^3$ is vacuum-infiltrated with a low-viscosity epoxy to fill open pores. Epoxy infiltration stabilizes the porous microstructure, enables planar sectioning, and supports phase separation, as the resin emits very low SE and BSE signals. In SEM images, epoxy-filled pores appear black, thereby enhancing the contrast between solid phases and enabling semi-automated segmentation.

Without infiltration, sputtered material can redeposit inside pores, and the curtaining effect may cause vertical streaking (270). The main challenge of infiltration is the formation of air bubbles, which may accumulate charge during imaging and hinder segmentation. To minimize bubble formation, Epofix epoxy (Struers; resin: hardener = 25:3 by weight) is used. The sample is

placed in a small vacuum chamber (≤ 100 mbar), where the epoxy is drawn into the structure. Maintaining reduced pressure for several minutes allows bubbles to escape before the pressure is gradually returned to ambient, resulting in nearly bubble-free infiltration.

The infiltrated sample is then cut to approximately $10 \times 10 \text{ mm}^2$ to remove excess epoxy. Grinding with coarse polishing paper is generally faster than cutting with a diamond saw. Subsequent polishing is performed with SiC papers of decreasing grit sizes (10 to $1 \mu\text{m}$), preparing two perpendicular cross-sections to ensure a sharp edge. Final polishing is performed using a diamond suspension. Improved sample stability can be achieved by producing twinned specimens, created by gluing two electrodes face-to-face. This approach also allows multiple regions to be prepared simultaneously, which is particularly advantageous when working with long-term operated cells (271, 272).

Finally, the sample is mounted on a SEM stub with conductive Ag paint and coated with a thin gold layer ($\approx 20\text{--}300 \text{ nm}$) to ensure electrical contact, reduce charging, and protect edges from streaking.

3.7.4.2 Focused Ion Beam Tomography

The operating principle of focused ion beam (FIB) systems is similar to that of SEM: both use a focused beam of charged particles (SEM: electrons; FIB: ions) under high vacuum. In FIB, ions are generated from a liquid gallium source, and the beam can be used not only for imaging but also for precise manipulation of the sample (273, 274, 275).

In FIB tomography, a high current ion beam (typically 100 pA – 20 nA for milling, $\sim 50 \text{ pA}$ for imaging at 30 kV) removes thin slices of the sample with a defined thickness ($20\text{--}50 \text{ nm}$, corresponding to the resolution in the slicing direction). After milling, SEM images are collected. Dual-beam systems, such as the Zeiss 1540 XB, tilt the electron and ion beams relative to each other ($\sim 54^\circ$) to allow automated slice-and-view imaging without tilting the sample. Hundreds of consecutive images are acquired, enabling reconstruction of volumes at least $15 \mu\text{m}$ deep.

Artifacts such as re-deposition, charging, curtaining, and shadowing can affect image quality. Re-deposition in porous structures is minimized by back-filling with epoxy resin, which stabilizes the structure, defines the cross-sectional area, and improves contrast between pores and electrode materials. Beam current, detector type, and preparation technique further influence image quality. Tilt correction and dynamic focusing are applied to ensure accurate cross-sectional imaging.

Two main acquisition modes are sequential slice-and-view, in which milling pauses for imaging, and continuous acquisition, in which images are captured during milling. Continuous mode is

faster but may introduce noise and beam interference. Careful preparation and optimized imaging parameters are therefore essential to minimize artifacts.

FIB tomography provides high spatial resolution (~ 3 nm) and strong material contrast, enabling quantitative 3D analysis of porous electrodes. It is destructive, limited in volume, and requires labor-intensive preparation and post-processing. Simultaneous use of multiple detectors allows complementary information to be combined, further enhancing data quality.

4 Results and Discussion

This chapter is divided into five sections. It begins with evaluating the different cells operating in the multi-cell test setup to clarify how measurements should be carried out. The next step is to characterize electrode performance using electrochemical and structural analyses. Sensitivity tests were carried out to identify the loss process within the electrode, thereby establishing an ECM. After the appropriate samples and test protocols were selected, the electrodes underwent designed accelerated stress tests. The corresponding results were analyzed using a novel data-processing method, enabling direct comparison of degradation behavior across different temperatures and humidity levels. Finally, mathematical and semi-empirical models were used to extrapolate the electrodes' long-term performance at 600 °C beyond 100,000 hours.

4.1 Test Method Validation Firstly, this section addresses the pseudo-inductive loop observed in the impedance spectra. A simplified physical model was developed to simulate this phenomenon, providing a new interpretation of this rare in SOFC but in other electrochemical systems widely reported behavior. Based on these findings, recommendations were made for applying the active-driven gas layer concept in the multi-cell test setup. The results of this section can be found in the publication (5).

4.2 Initial Performance and Microstructure of Ni/GDC Anodes with Varied Composition

A polarization resistance of 0.25 Ωcm^2 at 600 °C and 50% humidity is targeted (276), significantly lower than that of commercially available Ni/GDC electrodes. Cells fabricated at Forschungszentrum Jülich GmbH were delivered to KIT for comprehensive electrochemical and structural characterization. The results were used to evaluate the effectiveness of various fabrication approaches, such as screen printing and infiltration, as well as key parameters, including sintering temperature, particle size, and reduction protocols. Part of the results regarding initial characterization of cells from Ref1, V1.2, V6.1, and V6.12 are illustrated in the publication (3).

4.3 Electrochemical Characterization of Selected Ni/GDC Anodes To identify an effective degradation indicator for the electrode, analogous to the voltage for the stack, sensitivity tests were conducted to locate the loss processes within the electrode. The investigated parameter variations included temperature, steam, and hydrogen partial pressures, and different inert gas species. Up to five distinct processes were identified, four of which were assigned to known physical origins, while one mid-frequency process remained unidentified. The two electrode-related processes

were attributed to charge transfer and charge transport, whose coupling is described by the TLM (see Section 2.8.4). Consequently, the ECM was modeled as a TLM element in series with a resistive element R and three RQ elements. Among the TLM parameters, the charge-transfer resistance r_{ct} was selected as the degradation indicator. Part of the results of cells IS1-437_V6.1 and IS1-441_V6.5 are illustrated in the publication (3).

4.4 Accelerated Durability Tests at Elevated Temperatures It is necessary to identify both appropriate cell types and suitable stressor limits for AST to ensure that the same dominant aging mechanism applies under elevated stressors as under nominal operating conditions. This section presents and discusses the observed performance degradation at various temperatures and humidities, along with the corresponding microstructural changes. Cell variant V1.5a was selected as a representative sample for modeling. It was determined that testing at temperatures below 750 °C is necessary to ensure the validity of the accelerated aging methodology. Part of the results of cells IS1-424_V1.2_1, IS1-427_V1.2_1, IS1-429_V1.2_1, and cells IS1-437_V6.1, IS1-441_V6.5 are illustrated in the publications (4) and (3).

4.5 Aging Behavior Analysis and Modeling This Section introduces a novel data-processing method that enables direct comparison of cells aged under different conditions. In the absence of a physics-based model, several purely mathematical approaches and semi-empirical models were adopted, which successfully predicted electrode performance trends up to 10,000 h with an error of $\pm 7.56\%$ and up to 100,000 h with an error of $\pm 18.7\%$. A conference contribution that explains the data-processing method for standardization can be found in (11). The results of data interpretation and aging modeling are summarized in an unpublished contribution (7).

4.1 Test Method Validation

The cells IS1-454_V1.5a, IS1-454_V1.4a, and IS1-454_V1.2b presented in this section consist of an electrolyte and two screen-printed Ni/GDC electrode layers prepared from the usual Jülich paste and sintered at 1200, 1300, and 1400 °C, respectively. Cell IS1-456_V4.6, in contrast, consists of an electrode fabricated by two successive Ni infiltration steps into a GDC layer sintered at 1200 °C. All cells were equipped with contact layers composed of particles with a size of 0.5 μm . The results discussed in this section have been published in (5).

According to Section 3.4, the multi-cell test method could be validated via testing with identical cells and different cells, as shown in Figure 3.6(a, b). The test results of the former are discussed in Section 4.4.1.1. The efficiency of the test methodology itself is established for testing with several identical cells. This approach has the potential to save considerable resources in gas, energy, and time, making it a cost-effective testing method.

Another goal is to reduce the number of tests by assembling different cells and testing them simultaneously. This allows for a direct comparison of the performance and aging behavior of multiple cells in one experiment.

Figure 4.1(a) shows a rare characteristic in SOFC in the impedance spectrum of the electrode from IS1-454_V1.5a at 600 °C. Unlike the electrodes from IS1-454_V1.4a and IS1-454_V1.2b, its spectrum curves back at low frequencies, leading to an unexpected reduction in polarization resistance. The DRT analysis in Figure 4.1(b) further highlights this phenomenon, indicating a broader time constant distribution for the electrode primary process (3-100 Hz).

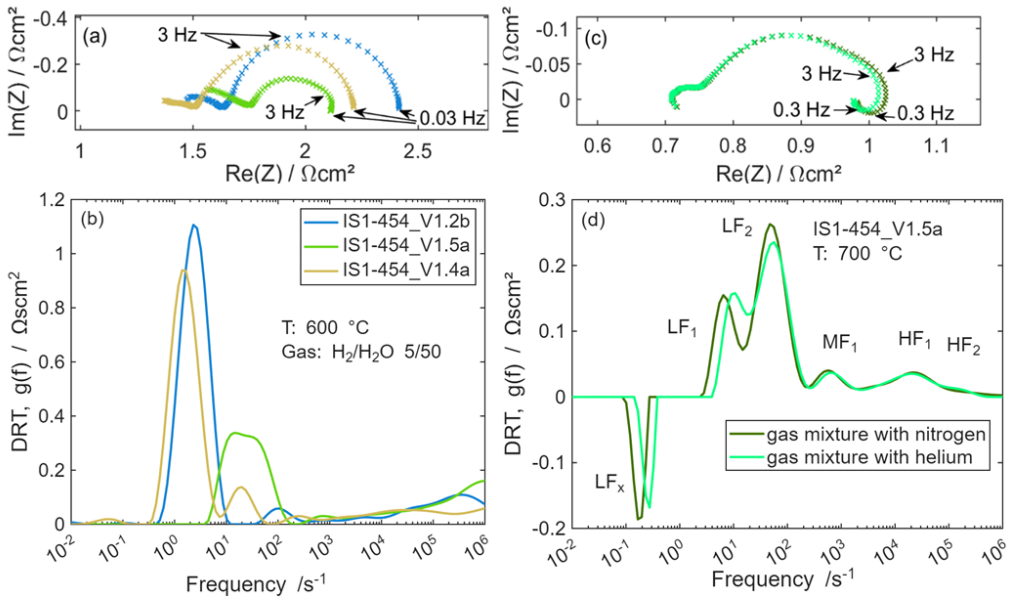


Figure 4.1: (a) Impedance spectra and (b) corresponding DRTs of electrodes from IS1-454_V1.4a, IS1-454_V1.5a, and IS1-454_V1.2b at 600 °C under 50% humidity in hydrogen. (c) Impedance and (d) DRT of electrode from IS1-454_V1.5a when alternating inert gases at 700 °C ($p_{\text{H}_2\text{O}} = 0.05$ atm, $p_{\text{H}_2} = 0.30$ atm). Schematic presentation of the cell positions in the setup is shown in Figure 3.6(b). Values are halved for single electrode evaluation. Adapted from (5).

Measurement artifacts were excluded by the characterization under alternating inert gases. As shown in Figure 4.1(c, d), a pseudo-inductive loop appears below 3 Hz in the impedance spectrum of the electrode from IS1-454_V1.5a at 700 °C when $p_{\text{H}_2\text{O}}$ is reduced to 0.05 atm by introducing N_2 or He . The corresponding DRT presents six peaks, labeled in order of increasing frequency: LF_x , LF_1 , LF_2 , MF_1 , HF_1 , and HF_2 . The LF_x peak, which corresponds to the inductive loop, is processed as a negative peak following the DRT calculation method established for PEM fuel cells at IAM-ET, KIT (277). Processes above 10 kHz, which are attributed to the electrolyte

and GDC/YSZ interface (196), remain unaffected by these low-frequency features and are not discussed further.

Under low steam content, the process LF_{1+2} (10–300 Hz) splits into two low-frequency peaks, LF_1 and LF_2 . The impact of alternating the inert gas between N_2 and He on these processes was investigated. Since H_2 and H_2O exhibit different diffusion coefficients in N_2 and He, and both gases are electrochemically inert, the observed changes in the LF_x and LF_{1+2} processes are attributed to changes in gas diffusion, according to (236). Consequently, we refer to these as a gas-concentration process to describe potentially complex gas-transport phenomena (278). Switching from N_2 to He reduces the absolute magnitude of the LF_x process, thereby decreasing its contribution to the overall R_{Pol} . A similar reduction is observed for the combined low-frequency processes LF_{1+2} .

4.1.1 Inductive Loop Dependency

Figure 4.2 illustrates the dependency of the impedance of electrode of IS1-454_V1.5a on variations in hydrogen (p_{H_2}) and steam (p_{H_2O}) partial pressure. An increase in p_{H_2} is correlated with a reduction in the ohmic resistance and a decrease in the magnitude of both the LF_x and LF_{1+2} processes. The former may be attributable to the p_{O_2} dependence of the GDC structure, which governs electronic conduction in the electrochemically inactive regions of the electrode. In contrast, the mid-frequency process demonstrates only a weak dependency on hydrogen content.

An increase in p_{H_2O} results in a strong negative dependency in the absolute magnitude of the LF_x process. Furthermore, as shown in Figure 4.2(c, d), the LF_1 peak shifts to higher frequencies under high steam content, causing it to overlap significantly with LF_2 . Due to this strong overlap, the individual dependencies of LF_1 and LF_2 on steam content cannot be conclusively determined. However, the overall magnitude of the combined LF_{1+2} process decreases. The MF process exhibits a weaker dependency on p_{H_2O} than the low-frequency features. However, this dependency is more obvious than its response to variations in p_{H_2} .

Several new features have appeared in the impedance spectra compared to the widely reported Nyquist plots on Ni/GDC symmetrical cells in a single-cell setup (238, 196). Given that the validation of the proposed multi-cell testing methodology is the key point, the emphasis will be on understanding the physicochemical origin of the observed low-frequency inductive loops and on developing a model that qualitatively reproduces this impedance feature.

Low-frequency pseudo-inductive loops are commonly observed in numerous electrochemical fields (279, 280, 281, 282, 283). The theoretical explanations for these features often points to mechanisms such as electrochemical adsorption/desorption, particularly through side reactions

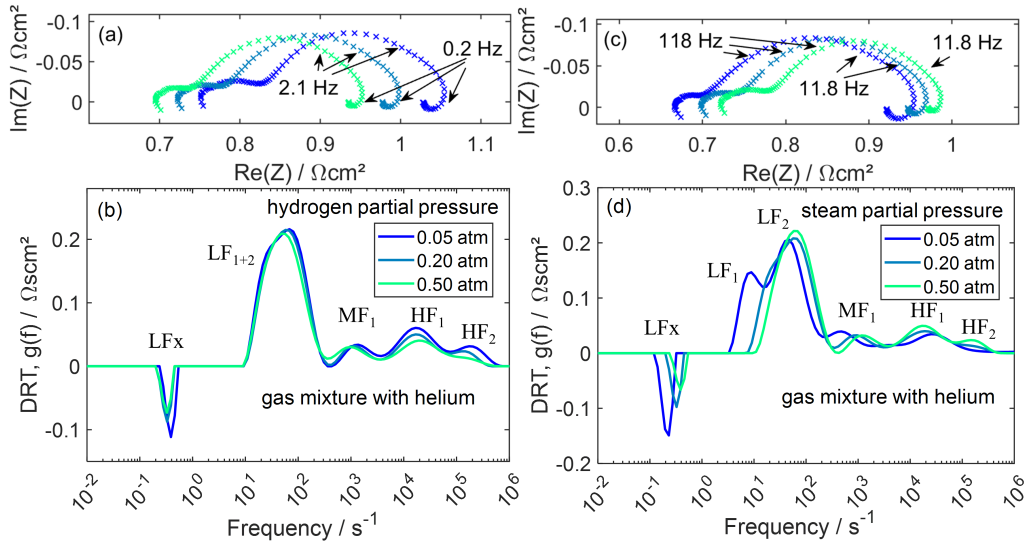


Figure 4.2: Impedance spectra and DRTs of the electrode of the cell from IS1-454_V1.5a at 700 °C under varying hydrogen (a, b) and steam (c, d) partial pressures. Helium is used as an inert gas. Values are halved for single electrode evaluation. Adapted from (5).

involving intermediate species (284, 285, 286, 287, 288, 289, 290), or to processes of metallic corrosion/dissolution (291, 292). In the field of solid oxide cells (SOCs), only a limited number of publications have discussed similar phenomena. For instance:

- T. Jacobsen et al. (293) observed this inductive loop phenomenon on Pt point electrodes formed on YSZ at 1000°C and attributed it to a current-induced activation mechanism with subsequent deactivation at equilibrium conditions.
- Guillaume Jeanmonod (294) associated the appearance of an inductive loop to possible modifications in electrochemical pathways resulting from the poisoning effects of chlorine on a solid oxide cell operated in co-electrolysis.
- Venkatesh Sarda (295) described this phenomenon on a Ni/YSZ anode half-cell, indicating a strengthening effect with increasing load. No clear explanation was given.
- W.G. Bessler (278) suggested a possible appearance of an inductive loop due to complex gas concentration loss, although this was not validated by experimental results.

4.1.2 Single- vs Multi-Cell Setup

To investigate the origin of the pseudo-inductive loop, a cell IS1-456_V4.6 was tested both in a conventional single-cell configuration and in a multi-cell assembly, sandwiched between two cells from V1.2 (which exhibited higher polarization resistance). A comparison of impedance spectra (Figure 4.3(a, b)) was performed after normalizing the real axis to zero at 10 kHz to exclude variations resulting from manual cell mounting procedures.

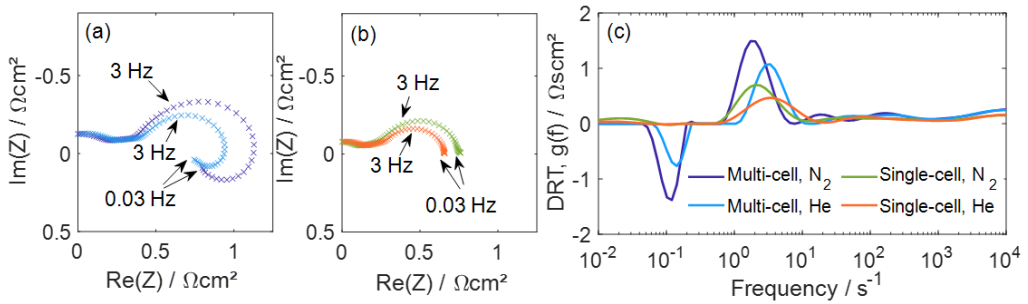


Figure 4.3: Impedance spectra of the cell IS1-456_V4.6 in (a) multi- and (b) single-cell setups under different inert gases ($p_{\text{H}_2\text{O}} = 0.05 \text{ atm}$, $p_{\text{H}_2} = 0.30 \text{ atm}$, 600°C). (c) Corresponding DRTs. Adapted from (5).

The inductive loop emerges exclusively in the multi-cell configuration. It is highly sensitive to inert-gas exchange, indicating that this feature is related to the active-driven gas layer environment rather than an intrinsic property of the cell. DRT analysis (Figure 4.3(c)) further reveals an enlargement of the combined LF_{1+2} process (1 Hz to 10 Hz) in the multi-cell setup. The enlarged negative contribution of the pseudo-inductive loop partially compensates for this enlargement. Given the dependence of LF_{1+2} on the type of inert gas, this enlargement is likely attributable to gas transport-related processes.

Notably, the polarization resistance increased from $0.67 \Omega\text{cm}^2$ in the single-cell setup to $0.75 \Omega\text{cm}^2$ in the multi-cell setup under an identical gas atmosphere when helium was used as the inert gas. This increase is mostly attributed to the enlarged LF_{1+2} processes, whose influence outweighs the compensatory effect of the inductive loop. Consistent with previous findings (238), the use of helium generally reduces polarization resistance by $0.05 \Omega\text{cm}^2$ in the multi-cell and $0.08 \Omega\text{cm}^2$ in the single-cell setup. These reductions correspond to gas diffusion losses of $0.0294 \Omega\text{cm}^2$ and $0.0473 \Omega\text{cm}^2$, under 800°C operation with a $\text{H}_2:\text{H}_2\text{O} = 50:50$ mixture. Both values exceed those reported for standard single-cell test configurations in (238).

The larger gas diffusion loss in the multi-cell setup may be influenced by the inductive loop and complex gas transport dynamics, while the higher loss in the single-cell setup may be partly due to structural properties of the electrode, such as an ultra-fine Ni nanostructure (particle size <

10 nm) resulting from infiltration, or due to absence of a forced flow normally available in a standard single-cell setup.

The lack of comprehensive process deconvolution complicates a detailed mechanistic interpretation. The new test method appears to introduce additional complexity in gas transport, likely including concentration-driven flow through the Ni-mesh and from the chamber atmosphere into the space between electrodes. A full understanding of the pseudo-inductive loop requires a model that accounts for a current for impedance measurement, the dynamics of reactant and product production and consumption, and the gas transport between two electrodes connected by the active-driven gas layer. In the following section, a simplified physical model is developed to explore and clarify the appearance of the low-frequency inductive loop.

4.1.3 Modeling and Simulation

The pseudo-inductive loop was observed in approximately 10% of tests in this work. It rarely appeared during the initial characterization but emerged predominantly during sensitivity tests under conditions of very low partial pressure of either steam ($p_{\text{H}_2\text{O}}$) or hydrogen (p_{H_2}).

To identify the prerequisites, all tests exhibiting this loop were systematically reviewed to compare operating conditions, the corresponding cell's properties, and the state of its neighboring cells. This analysis revealed that the pseudo-inductive loop occurred consistently only when a high-performing cell was sandwiched between two lower-performing cells. When identical cells are assembled, no inductive loops are ever observed.

A plausible explanation is that it stems from differences in polarization resistance and chemical capacitance among electrodes in adjacent cells. The fundamental equivalent circuit for an electrode (Figure 4.4(a)) consists of a charge-transfer resistance (R_i) parallel to a chemical capacitance (C_i). Under an ac excitation during impedance measurements, the supplied current splits at the electrode interface: one component passes through the charge-transfer resistance, while the other charges the chemical capacitance of the GDC phase.

The Faradaic current component is associated with the electrochemical oxidation/reduction of gas species ($\text{H}_2/\text{H}_2\text{O}$), thereby altering the local gas composition. Conversely, the non-Faradaic component accumulates charge within the interfacial chemical capacitance without participating in surface reactions. From a mechanistic perspective, oxygen ions migrating through the 8 YSZ electrolyte may either: (1) undergo charge transfer reactions with hydrogen or steam, altering gas composition, or (2) be incorporated into the GDC lattice through non-Faradaic processes, thus remaining electrochemically inactive with gaseous species in the electrode and Ni-mesh.

The cell-level equivalent circuit consists of two RC elements (representing electrode processes) in series with an ohmic resistance (R_0) that accounts for ionic/electronic transport losses in the electrolyte and inactive electrode. For the three-cell mechanical assembly, the equivalent circuit model consists of three such units connected in series (Figure 4.4(a)), with negligible resistance contributions from interposed Ni-meshes.

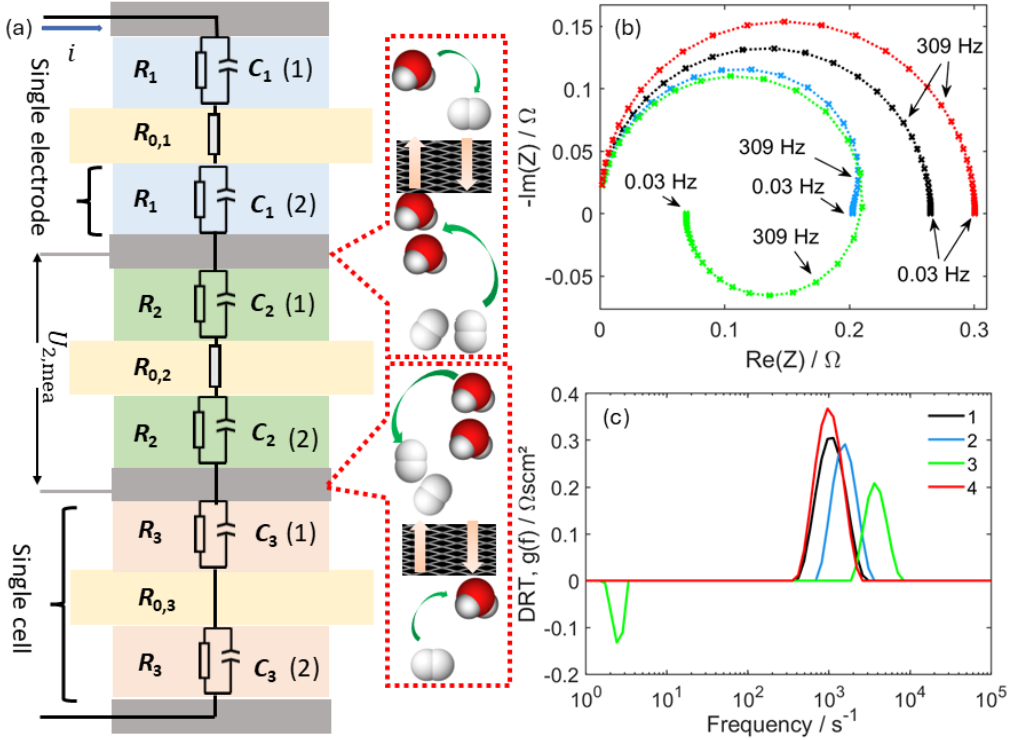


Figure 4.4: (a) Simplified equivalent circuit for three cells in series applying the active-driven gas layer. Ni-meshes and current collectors are denoted in gray, 8YSZ electrolytes are yellow, and electrodes of cells 1–3 are in blue, green, and orange. (b) Simulated impedance and (c) corresponding DRTs of cell 2 under varying neighboring cell performance. Adapted from (5).

Assuming identical chemical capacity, the current through the charge-transfer resistances is thus the same across the identical electrodes. This current is proportional to the speed of fuel production/consumption. During a certain time unit, the hydrogen/water steam produced/consumed equals the hydrogen/steam consumed/produced between the two electrodes separated by a nickel mesh. This ideal situation is discussed in Figure 3.4 in Section 3.3.1. Assuming rapid gas transport in the nickel mesh and the porous electrodes, a small gas concentration gradient between

the electrodes can be continuously evened out and neglected. Therefore, the atmosphere near the electrodes is always the same as the preset gas compositions in the chamber.

However, the assumed quasi-equilibrium and symmetry are disrupted if neighboring electrodes exhibit different performances. As shown in Figure 4.4(a), three different cells are connected in series with only Ni-meshes in between. For simplicity, the gas concentration process between two neighboring electrodes is assumed to be limited to perpendicular transport within the Ni mesh and to occur very quickly. No in-plane gas exchange to the chamber is considered. As a result, the gas compositions in the neighboring electrodes are identical, such as position (2) of cell 1 and position (1) of cell 2. The same value is applied to the chemical capacitance C_i for all 3 cells, since they depend on the GDC amount in the electrodes. With the electrode of cell 2 superior compared to the other 2 cells ($R_2 < R_1, R_3$), the ac-current flowing through the charge-transfer resistances is largest on R_2 .

Assuming the current flowing through cells 1 to 3 during positive current half-cycles:

- The produced hydrogen in the electrode (2) of cell 1 is less than that consumed at the electrode (1) of cell 2.
- The consumed steam in the electrode (2) of cell 1 is less than that produced at the electrode (1) of cell 2.

As a result, an excess of steam/ lack of hydrogen compared to the preset atmosphere in the chamber occurs in the assumed active driven gas layer, as indicated in the top red dialog in Figure 4.4(a). At the position indicated by the bottom red dialog window, an excess of hydrogen/ a lack of steam is present. During the negative current half-cycles, the opposite occurs. Thus, the superior cell 2 experiences asymmetric gas compositions in its electrodes during impedance measurement, generating a Nernst voltage described by a modification of Equation 2.5:

$$U_N = \frac{R_g T}{2F} \ln \left(\frac{\sqrt{p_{O_2, \text{top electrode}}}}{\sqrt{p_{O_2, \text{bottom electrode}}}} \right) \quad (4.1)$$

where $p_{O_2, \text{top electrode}}$ and $p_{O_2, \text{bottom electrode}}$ are the partial pressures of oxygen at the top and bottom electrodes of cell 2. The Nernst voltage across cell 2 would be zero if the gas compositions at both electrodes were identical. The unsymmetrical atmosphere results in a non-zero Nernst voltage U_N .

The measured voltage across cell 2 during the impedance measurement (ohmic resistance neglected) can be expressed as:

$$U_{2,\text{mea}} = \frac{2R_2}{1 + j\omega R_2 C_2} \cdot i + U_N \quad (4.2)$$

The measured impedance of cell 2 is:

$$Z_{2,\text{mea}} = \frac{2R_2}{1 + j\omega R_2 C_2} + \frac{U_N}{i} \quad (4.3)$$

To simplify the derivation and calculation processes, several assumptions were made:

- All cells are measured under OCV. The only current source is the ac activation signal from the impedance analyzer for impedance measurement.
- As the thickness of the Ni-mesh (200 μm) is dominant, the thickness of electrodes ($\sim 10 \mu\text{m}$) can be neglected, .
- The Ni-mesh is assumed to be successfully "sealing" the space between two neighboring electrodes. Thus, no in-plane exchange to the chamber is considered. The atmosphere in the "sealed" space is the same as the preset atmospheric conditions in the chamber before the start of every impedance measurement.
- The "sealed" space has an area of 1 cm^2 , the same as the active electrode area, and a thickness of 200 μm , corresponding to the thickness of the Ni-mesh, with a porosity of 0.5.
- The gas transport is assumed to be perpendicular and ultra-fast, such that no gas concentration gradient is present within the "sealed" space.
- The targeted inductive loop features fall in the low frequency ranges, where the data acquisition of impedance measurement was carried out via sampling. Thus, the simulation will be performed by integration over one period and averaging to mimic the digital reading procedure.

The current flowing through the cells is:

$$i = I \cdot e^{j\omega t} \quad (4.4)$$

where t represents the time and I the amplitude of the ac current.

According to Kirchhoff's law, the current flowing through each charge-transfer resistance can be calculated:

$$\begin{aligned} I_{R_1} &= \frac{1}{R_1} \cdot \frac{1}{\frac{1}{R_1} + j\omega C_1} \cdot I \cdot e^{j\omega t} \\ I_{R_2} &= \frac{1}{R_2} \cdot \frac{1}{\frac{1}{R_2} + j\omega C_2} \cdot I \cdot e^{j\omega t} \\ I_{R_3} &= \frac{1}{R_3} \cdot \frac{1}{\frac{1}{R_3} + j\omega C_3} \cdot I \cdot e^{j\omega t} \end{aligned} \quad (4.5)$$

In the case of an ac current, the electrode where hydrogen is consumed will produce hydrogen in the next half-period. Taking position (2) of cell 1 as an example, the rate of change in the amount of hydrogen $n_{H_2,1(2)}$ and steam $n_{H_2O,1(2)}$ is:

$$\frac{dn_{H_2,1(2)}}{dt} = -\frac{dn_{H_2O,1(2)}}{dt} = \frac{I_{R_1}}{2F} \quad (4.6)$$

The change in the amount of hydrogen/water steam is thus:

$$\Delta n_{H_2,1(2)} = -\Delta n_{H_2O,1(2)} = \int \frac{I_{R_1}}{2F} dt \quad (4.7)$$

Similarly, in position (1) of cell 2:

$$-\frac{dn_{H_2,2(1)}}{dt} = \frac{dn_{H_2O,2(1)}}{dt} = \frac{I_{R_2}}{2F} \quad (4.8)$$

$$-\Delta n_{H_2,2(1)} = \Delta n_{H_2O,2(1)} = \int \frac{I_{R_2}}{2F} dt \quad (4.9)$$

The net change in the amount of hydrogen and steam in the "sealed" space between cells 1 and 2 is.

$$\Delta n_{H_2,1-2} = -\Delta n_{H_2O,1-2} = \Delta n_{H_2,1(2)} + \Delta n_{H_2,2(1)} \quad (4.10)$$

The total gas amount in the "sealed" space between cells 1 and 2 is calculated based on the ideal gas law:

$$n_{\text{sealed}} = A \cdot d \cdot \varepsilon \cdot \frac{P}{R_g \cdot T} \quad (4.11)$$

A denotes the active area of the electrode (1 cm^2), d and ε the thickness of Ni-mesh ($200 \text{ }\mu\text{m}$) and the porosity (0.5), and P the pressure of the gas composition (same as the atmosphere in our setup). This value applies to all the "sealed" spaces between the electrodes.

The mole fractions of hydrogen and steam preset for the chamber are x_{H_2} and $x_{\text{H}_2\text{O}}$. Therefore, the amounts preset for each component are:

$$\begin{aligned} n_{\text{H}_2, \text{preset}} &= n_{\text{sealed}} \cdot x_{\text{H}_2} \\ n_{\text{H}_2\text{O}, \text{preset}} &= n_{\text{sealed}} \cdot x_{\text{H}_2\text{O}} \end{aligned} \quad (4.12)$$

The amounts of hydrogen and steam between cells 1 and 2 during the impedance measurement are:

$$\begin{aligned} n_{\text{H}_2, 12} &= n_{\text{H}_2, \text{preset}} + \Delta n_{\text{H}_2, 1-2} \\ n_{\text{H}_2\text{O}, 12} &= n_{\text{H}_2\text{O}, \text{preset}} + \Delta n_{\text{H}_2\text{O}, 1-2} \end{aligned} \quad (4.13)$$

The same procedure is applied to the "sealed" space between cells 2 and 3. Based on Equation 4.1, the Nernst voltage across cell 2 can be calculated considering the law of mass action:

$$U_{\text{N},2} = \frac{R_{\text{g}}T}{2F} \ln \left(\frac{n_{\text{H}_2\text{O},23} \cdot n_{\text{H}_2,12}}{n_{\text{H}_2,23} \cdot n_{\text{H}_2\text{O},12}} \right) \quad (4.14)$$

The measured impedance of cell 2 according to Equation 4.3 is:

$$Z_{2, \text{mea}} = \frac{2R_2}{1 + j\omega R_2 C_2} + \frac{R_{\text{g}}T}{2F \cdot I \cdot e^{j\omega t}} \ln \left(\frac{n_{\text{H}_2\text{O},23} \cdot n_{\text{H}_2,12}}{n_{\text{H}_2,23} \cdot n_{\text{H}_2\text{O},12}} \right) \quad (4.15)$$

The simulated impedance of cell 2 is the integration of the impedance and then averaged over the integrated time period :

$$Z_{2, \text{mea}, \text{sim}} = \frac{\int_0^{\frac{2\pi}{\omega}} Z_{2, \text{mea}} dt}{\frac{2\pi}{\omega}} \quad (4.16)$$

For simulation, the integration time is chosen to be one full period $\frac{2\pi}{\omega}$. The frequencies of measured points are the same as those in the real test. The MATLAB[®] code for impedance simulations is available in Appendix A.4.

The first simulation focuses on recreating the pseudo-inductive loop in impedance. For faster calculations, all chemical capacitances were assumed to be 0.07 F , and ohmic resistances were

neglected. The impedance of cell 2 was simulated with two identical neighboring cells (Case 1) and two inferior neighboring cells (Case 2), using the parameters listed in Table 4.1.

Table 4.1: Model parameters for simulating the impedance of cell 2 in Figure 4.4(a) at 700 °C in a gas composition of steam and hydrogen (50:50).

Case	$p_{\text{H}_2\text{O}}$ (atm)	p_{H_2} (atm)	I (A)	T (°C)	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)	C_i (F)
1					0.13	0.13	0.13	0.07
2	0.5	0.5	0.05	700	0.25	0.13	0.25	0.07
3					0.50	0.13	0.50	0.07
4					0.06	0.13	0.06	0.07

As shown in Figure 4.4(b), the simulated impedance arc forms a perfect semicircle where all three cells exhibit identical performance. The polarization resistance of cell 2 is 0.26 Ω , twice the charge-transfer resistance R_2 .

In case 2, the simulated arc deviates from a semicircle. The curve in the low-frequency range bends backward towards smaller values on the real axis, leading to a reduced polarization resistance of 0.20 Ω . The low-frequency peak LF_{1+2} moves towards higher frequencies and decreases in amplitude.

Until Case 2, no inductive loop was observed. After further enlargement of R_1 and R_3 to approximately four times that of R_2 (Case 3), a pseudo-inductive loop emerges in the low-frequency region, resulting in a polarization resistance of only 0.069 Ω .

Case 4 considers the scenario in which cell 2 performs worse than cells 1 and 3, as highlighted in red in Figure 4.4(b, c). This results in an increased polarization resistance of 0.30 Ω and the absence of an inductive loop. This indicates the questionable reliability of impedance measurements for cells adjacent to inferior cells. This might lead to an overestimation of the polarization resistance.

After successfully reproducing the inductive loop, further simulations were performed to investigate the theoretical influence of the partial pressures of steam and hydrogen. The parameters used to simulate the cell impedance under different gas compositions are summarized in Table 4.2. These parameters were obtained by fitting the measured impedances of the three cells IS1-454_V1.4a, IS1-454_V1.5a, and IS1-454_V1.2b using RQ elements to represent the process in the 10–100 Hz frequency range. The three cells in Figure 3.6(b) correspond to cells 1, 2 and 3 in Figure 4.4(a). To reduce the simulation effort, three partial pressure values for both steam and hydrogen were selected, mimicking the identical atmosphere shown in Figure 4.2.

The measurements were affected by gas composition asymmetry, likely present in all three cells. The capacitances of all three cells were set equal to that of the cell IS1-454_V1.4a to simplify the

calculation procedure. Furthermore, the estimated resistance of this cell was applied to both cells 1 and 3. All ohmic resistances ($R_{0,i}$) are neglected (set to zero).

Table 4.2: Model parameters for simulating impedance of the cell 2 in Figure 4.4(a).

I (A)	$p_{\text{H}_2\text{O}}$ (atm)	p_{H_2} (atm)	R_1, R_3 (Ω)	C_i (F)	R_2 (Ω)
0.05	0.05	0.30	0.45	0.090	0.24
	0.20		0.37	0.075	0.21
	0.50		0.33	0.069	0.18
	0.30	0.05	0.33	0.069	0.18
		0.20	0.32	0.069	0.18
		0.50	0.31	0.068	0.18

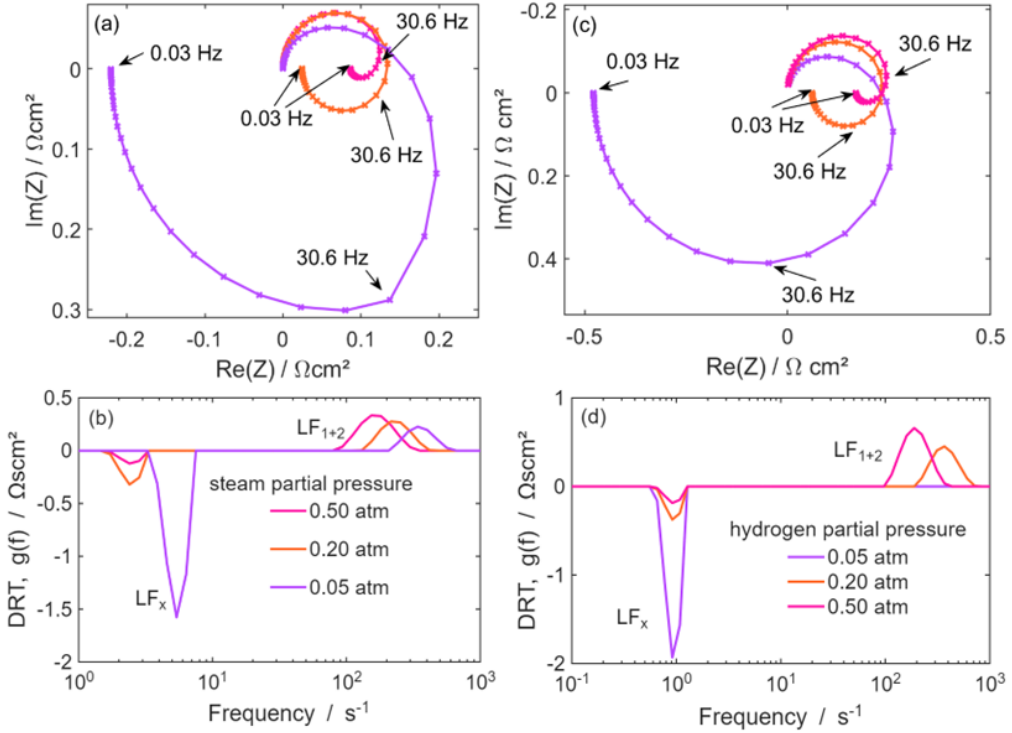


Figure 4.5: (a) Simulated impedances and (b) corresponding DRTs of cell 2 at 700 °C under varying steam partial pressure from 0.05-0.50 atm, while keeping hydrogen partial pressure constant at 0.30 atm. Adapted from (5). (c) Simulated impedances and (d) corresponding DRTs of cell 2 at 700 °C under varying hydrogen partial pressure from 0.05-0.50 atm, while keeping steam partial pressure constant at 0.30 atm.

A pseudo-inductive loop consistently emerges in all simulations, as shown in Figure 4.5(a, c). As the steam partial pressure increases, the magnitude of the inductive loop decreases, consistent with the behavior seen in Figure 4.2(d). The endpoint at the lowest frequency shifts towards higher values on the real axis, indicating an increase in polarization resistance measured by EIS. The capacitive semicircle at higher frequencies, representing the RC behavior of the electrode, is affected at low $p_{\text{H}_2\text{O}}$ values. The arc flattens, and the intersection with the real axis moves towards larger values. No splitting of LF_{1+2} or shift of LF_x towards lower frequencies is observed.

Similar trends are observed in the simulations as a function of hydrogen partial pressure. The inductive peak enlarges as the hydrogen partial pressure decreases from 0.50 to 0.20 atm. When this parameter is further reduced to 0.05 atm, the inductive loop increases drastically, contributing approximately $-0.75 \Omega\text{cm}^2$ to the polarization resistance. The effect of hydrogen content appears to be more pronounced in the low-concentration region than that of steam. In contrast, experimental measurements suggest that the influence of steam is stronger, as shown in Figure 4.2.

A negative polarization resistance was observed in experimental measurements on V4.4 cells in test IS1-453. Furthermore, the influence of alternating inert gas types, as illustrated in Figures 4.1 and 4.3, cannot be described by the established model, as gas diffusion speed is assumed to be ultra-fast. The model does not include a term representing gas transport between two electrodes connected via the active-driven gas layer.

The deviations between simulation and experiment can be attributed to the simplified electrochemical description of the electrodes and the neglect of complex gas transport phenomena. Dynamic gas transport between neighboring electrodes due to concentration gradients, as well as between the chamber and the "sealed" space in the Ni mesh separating the electrodes, is expected to depend on the inert gas species. Furthermore, the chemical capacitance of GDC is modeled as an ideal capacitance, neglecting nonlinearities and the distinct dynamic behavior associated with oxygen ion diffusion in GDC.

Summary

The multi-cell test methodology has proven highly effective for testing multiple identical cells simultaneously, thereby improving statistical reliability while substantially reducing time and resource costs. However, strict limitations must be taken into account when testing non-identical cells using this approach. Differences in electrode performance can lead to deviations in gas composition across a cell, resulting in an additional time-dependent voltage term. If neighboring cells perform worse, this effect may generate a pseudo-inductive loop in the impedance spectra. Whereas when better, the impedance arc may expand. In both scenarios, the measured polarization resistance is distorted.

The observations and modeling approach presented in this section explain one type of the widely reported pseudo-inductive loops in electrochemistry. Nonetheless, further investigations and the development of a multiphysics model that couples electrochemical reactions with complex gas-transport processes are required to explain the observed impedance behavior fully. To avoid the asymmetry and complexity that could compromise the reliability of impedance measurements, only identical cells or cells with similar polarization resistances were assembled and measured simultaneously in this study.

4.2 Initial Performance and Microstructure of Ni/GDC Anodes with Varied Composition

The initial characterization consists of impedance measurements at 600 °C after reduction and structural analysis of the beginning-of-life (BoL) state. A comparative evaluation of different cells allows the influence of fabrication parameters to be assessed, including sintering temperature, infiltration concentration, and contact-layer particle size. Cells exhibiting excellent performance, high reproducibility, and mechanical robustness, later with clearly identified electrode processes (Section 4.3), will be selected for subsequent investigations. A more detailed description of the cell variants is shown in A.2.

4.2.1 Initial Cell Performance

4.2.1.1 Cells Reduced at 800 °C

The initial batch of cells was fabricated using electrode paste formulations designed for anode-supported cells operated at 800 °C at FZJ. Consequently, the standard FZJ reducing protocol at 800 °C, previously validated to provide a stable electrode microstructure and reliable electrochemical performance, was applied.

A representative impedance spectrum with the corresponding DRT is presented in Figure 4.6(a, b). The impedance spectrum exhibits two prominent arcs (Figure 4.6(a)). The dominant arc, located at low frequencies, accounts for the largest fraction of the total polarization resistance, as confirmed in the DRT plot (Figure 4.6(b)). A second arc, observed in the 2–30 Hz frequency range, represents the next most significant resistive process. Both features consistently appear in all tested cells and together account for the majority of the polarization resistance.

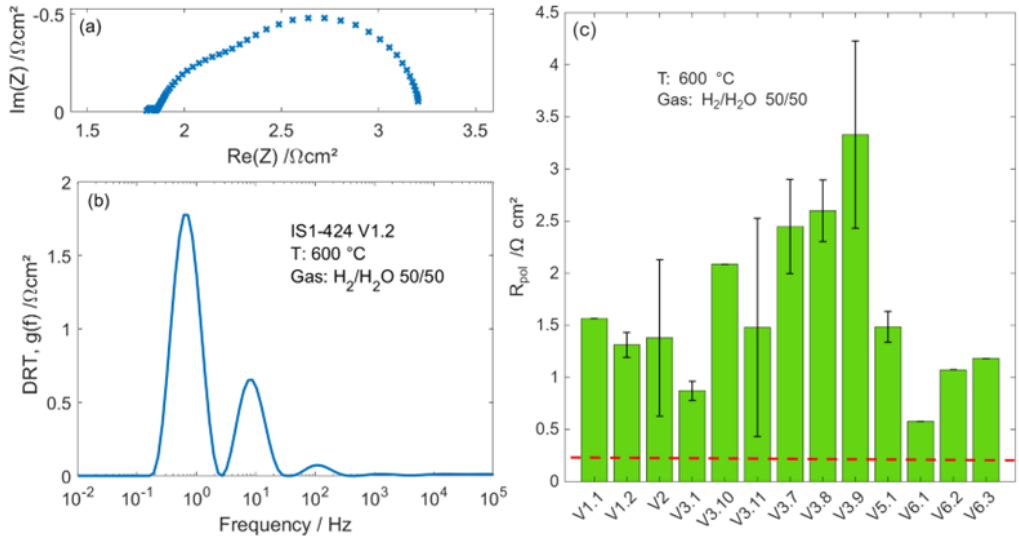


Figure 4.6: An example of general impedance (a) and corresponding DRT (b) of a Ni/GDC electrode with YSZ electrolyte at 600 °C with 50% steam in hydrogen, recorded from the cell IS1-424_V1.2_1. Impedance halved for single electrode evaluation. (c) An overview of the average initial polarization resistances under nominal conditions. The red dashed line indicates the target polarization resistance of $0.25 \Omega\text{cm}^2$ (276). No error bar indicates a single test result.

In some cases, additional features appeared in the very low- and high-frequency regions, which are discussed in Section 4.3. For quantification, the polarization resistance was defined as the difference between the high-frequency intercept on the real axis (or the real value at 10,000 Hz) and the maximum impedance. The values for all cells are summarized in Figure 4.6(c), with reproducibility indicated by error bars.

The ohmic resistance largely depends on the cell structure, including layer sequence, thickness, and the contact layer, leading to different values across cells. It should be noted that the symmetrical cells employed in this work serve as model systems designed to isolate the anode's loss processes from those of the cathode. The high ohmic resistance and its degradation predominantly arise from the thick supporting electrolyte and are therefore not relevant to the behavior in practical fuel electrodes or in metal-supported cells. Moreover, the large magnitude of this resistance and its intrinsic degradation can overshadow any potential ohmic degradation associated with the electrodes. Consequently, variations in ohmic resistance are not the primary focus of this study and are only briefly addressed where relevant. This consideration applies throughout the following discussion.

The polarization resistance of cells from V2, V3.1, V3.7, V3.8, V3.9 and V3.11 exhibits deviations exceeding 10%. The cells from V2 were produced using an invalid sintering protocol, which was

later optimized for the V1.5 cell variants. The cells in the V3 variant mentioned above experienced electrode delamination. Large pores and an inhomogeneous phase distribution were observed. The random electrode microstructure led to unstable electrochemical performance.

The infiltration-based V6 variants showed the best performance, followed by the screen-printed V1 and V2 variants. In the V6 variants, higher sintering temperatures increase polarization resistance, likely due to Ni particle coarsening and the resulting loss of active surface area. Among the screen-printed V1 variants, V1.2 cells outperformed V1.1, suggesting that the thinner electrode layer in V1.1 was insufficient for optimal electrode activity. The minimum necessary electrode thickness, equal to the penetration length, is given in (65). The V3 and V5 variants, produced with fine Ni and GDC powders, showed the weakest performance (except V3.1). The high sintering and reduction temperatures applied to these cells may have caused excessive agglomeration or partial sintering, leaving final particle sizes comparable to those of the V1 electrodes, thus canceling the benefit of finer precursors. Frequent delamination hindered post-test analysis and indicated poor stability.

Overall, none of the cells reduced at 800 °C achieved the target polarization resistance of $0.25 \Omega\text{cm}^2$ (red dashed line in Figure 4.6(c)). These limitations in performance and stability motivated further optimization of the electrode microstructure, including modifications to the interlayer and contact layer, adjustments to the sintering and infiltration steps, and variations in the reduction temperature.

4.2.1.2 Cells Reduced at 650 °C

Structural analysis of the screen-printed cells reduced at 800 °C (Section 4.2.2) revealed a coarse microstructure. To improve initial electrode performance at 600 °C, an intermediate reducing protocol at 650 °C was introduced. The initial characterization results are presented in Figures 4.7(a-c), categorized by fabrication method.

Infiltration generally produced the best-performing cells, with 7 of 13 variants reaching the targeted initial electrode performance and showing moderate reproducibility. Most infiltration-based cells showed good reproducibility, except for cells from V6.11 and V6.12, which suffered from electrode delamination and pronounced mechanical instability. In contrast, cells fabricated by screen printing with fine-particle pastes performed less effectively. However, two subvariants met the requirement, indicating that optimizing particle size, solvent composition, and thermal treatment is essential. In this category, only variant V5.1 showed deviations exceeding 10%, which can be attributed to inhomogeneities in the electrode microstructure.

None of the cells produced with the usual Jülich paste achieved the required performance. The best-case variant, V1.5a, exhibited an average polarization resistance of $0.29 \Omega\text{cm}^2$, indicating the limitations of conventional screen printing. The deviations of the cells from Ref1 and V1.5a exceeded 10%. In the former case, this is attributed to the limited number of tested cells (two samples). In the latter case, the deviation likely originated from the relatively dry paste. Impedance analysis revealed that these differences mainly arose in the frequency range above 10,000 Hz, where the dominant contributions are associated with interfacial and electrolyte-related processes. Thus, the reproducibility of the electrodes of V1.5a can still be considered excellent.

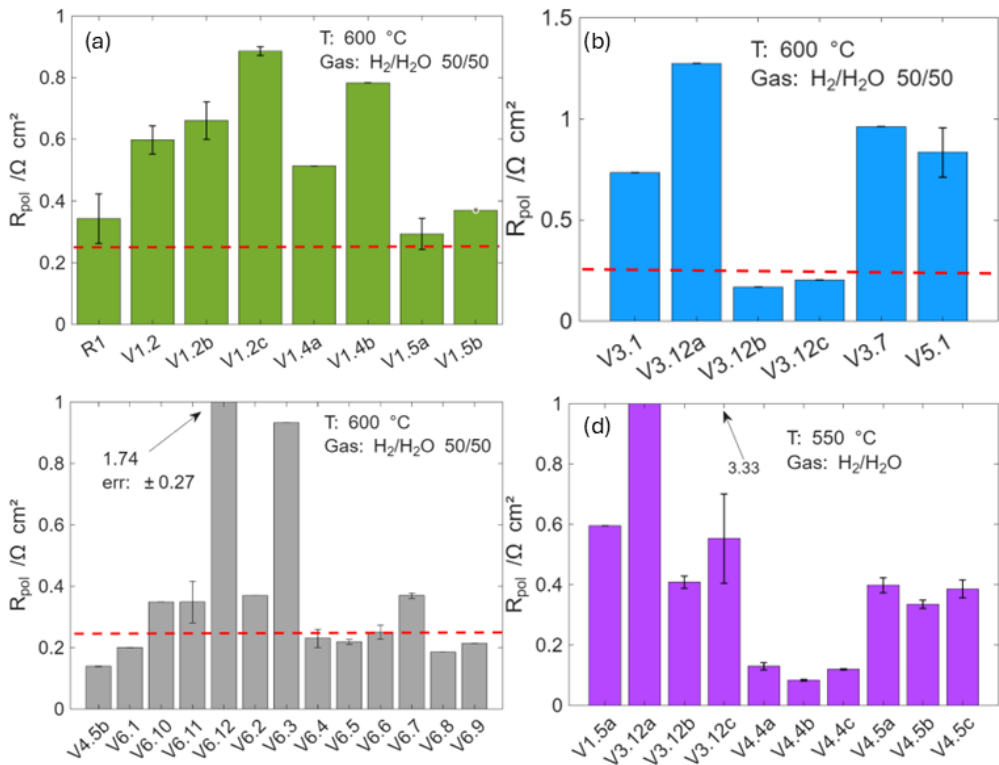


Figure 4.7: Summary of initial polarization resistances at 600 °C of cells from (a) usual Jülich Paste, (b) paste consisting of fine particles, (c) infiltration reduced at 650 °C, and initial polarization resistances at 550 °C from (d) cells reduced at 550 °C. The bars without error bars indicate a single test result. Adapted from (7).

A comparison between reduction at 800 °C and 650 °C reveals significant initial performance improvements, as presented in Figure 4.8. The polarization resistance of electrodes from V1.2 decreased from 1.31 to $0.60 \Omega\text{cm}^2$ (−54.2%). For variant V3.1, the value decreased from 0.87 to

0.73 Ωcm^2 (-12%); for V6.1, from 0.58 to 0.20 Ωcm^2 (-65%); for V6.2, from 1.07 to 0.37 Ωcm^2 (-65%); and for V6.3, from 1.18 to 0.93 Ωcm^2 (-22%). Similar improvements were also observed in V3.7 (-60%) and V5.1 (-33%). These results demonstrate that lowering the reduction temperature to 650 °C markedly enhances the initial performance regardless of fabrication method.

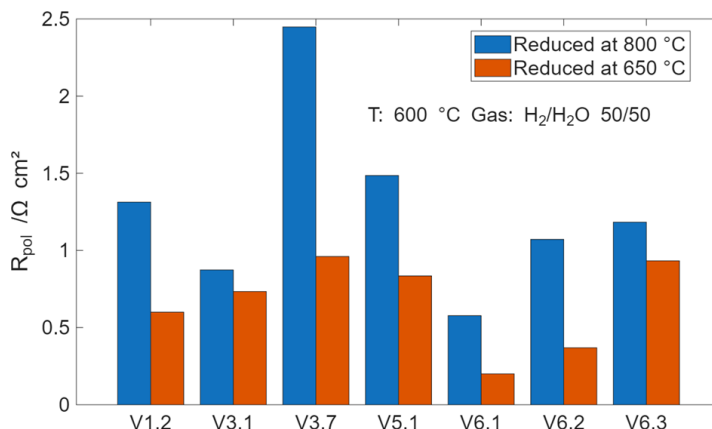


Figure 4.8: Comparison of the initial polarization resistance of electrodes reduced at 800 and 650 °C.

As shown in Figure 4.7(a), increasing only the sintering temperature (for example, cells from V1.5a, V1.4a, and V1.2b) resulted in higher polarization resistances, likely due to particle coarsening. The use of a contact layer with larger Ni particles (1.4 μm for V1.2c, V1.4b and V1.5b) resulted in poorer performance compared to cells with finer contact layers (V1.2b, V1.4a and V1.5a). Possible reasons include better adhesion and a larger activated electrode area for the latter case. The impact of the interlayer can be seen by comparing cells from V1.2 and V1.2b, where its absence led to a slight increase of 0.06 Ωcm^2 . Improved adhesion and enhanced ionic and electronic conduction may account for this difference.

An unusual performance was observed in cells from Ref1, which contained a GDC layer and a Ni contact layer. Despite being sintered at the same temperature as V1.4a and having no intentionally added Ni in the electrode, they outperformed cells from V1.4a, which had a higher Ni content. To investigate this unexpectedly superior behavior of the seemingly “Ni-free” electrode, structural analyses including SEM and EDS were performed. EDS mapping revealed that approximately 4% Ni was present within the GDC layer of Ref1, although no Ni-related features were visible in SEM images. This Ni most likely originated from the contact layer via surface diffusion during reduction, thereby activating the GDC surface and enhancing electrochemical performance (79). Although a similar diffusion mechanism may have occurred in cells of V1.4a, its electrode contains significantly less GDC (40% vs. 70% by volume fraction), resulting in less DPB. Moreover, no

evidence of Ni percolation was observed, indicating that the electronic conductivity remained limited to the GDC phase. Assuming that electrochemical activity in both variants is dominated by DPB, the lower GDC content of V1.4a accounts for its inferior performance.

For the V3 variant, several paste formulations with tuned particle size and material weight fraction were investigated. As shown in Figure 4.7(b), a compromise between performance and mechanical stability became apparent. Cells from V3.7 and V5.1 exhibited good mechanical stability but high polarization resistances, whereas cells from V3.1 displayed better performance but suffered from delamination. After further recipe optimization, the variant V3.12 demonstrated both reliable mechanical stability and excellent performance at 600 °C. In this variant, V3.12a cells exhibited the weakest performance, likely due to strong sintering at 1400 °C, which destroyed the fine electrode structure. Cells from V3.12b achieved a polarization resistance of $0.168 \Omega\text{cm}^2$, probably due to a fine electrode structure preserved at moderate sintering temperatures. However, at an even lower temperature (980 °C), cells from V3.12c exhibited slightly worse performance. Structural analysis indicated insufficient percolation of the GDC phase.

Infiltrating Ni into a GDC scaffold (V4) yielded superior results compared to infiltrating GDC into a Ni backbone (V6) (Figure 4.7(c)). Cells from V4.5b with 2 infiltration steps achieved the lowest polarization resistance of $0.14 \Omega\text{cm}^2$. Extensive efforts were devoted to exploring the limits of variant V6. The best polarization resistance achieved was $0.18 \Omega\text{cm}^2$, representing a six-fold improvement over the best results previously reported in the literature (126, 127, 128) and thereby pushing the limits of this method. Increasing the sintering temperature of the Ni backbone consistently led to higher polarization resistance under the same number of infiltration steps, most likely due to reduced TPB density resulting from Ni particle coarsening. The only exception was V6.4. This could be attributed to less successful Ni percolation.

Due to the limited number of cells, the influence of the infiltration step on variant V6 cannot be reliably evaluated. Nevertheless, structural analysis consistently revealed that the GDC phase uniformly filled the pore spaces between Ni particles, indicating that infiltration saturation might have been achieved in all samples. Given the comparable initial polarization resistances for cells from V6.1, V6.5, and V6.8, measured to be 0.20, 0.22, and $0.19 \Omega\text{cm}^2$, respectively, they are presumed to have similar initial electrode structures. Their long-term degradation behavior will be compared in detail in Section 4.4.

4.2.1.3 Cells Reduced at 550 °C

Cells from V3.12 and V4 exhibited a very fine Ni or GDC structure that agglomerated significantly even at 600 °C. To investigate the influence of nanoparticles, an extra-fine reducing

protocol at 550 °C was applied. The initial electrochemical characterization at 550 °C is shown in Figure 4.7(d), including a cell IS1-452_V1.5a as reference.

At identical sintering temperatures, the infiltration-based V4 cells exhibited the lowest polarization resistance, followed by cells from V3.12b and V3.12c (fine-particle paste), V1.5a (usual Jülich paste), and V3.12a (fine-particle paste sintered at 1400 °C).

Within the V4 variant, decreasing sintering temperature (V4.4a/b/c at 1200 °C and V4.5a/b/c at 1300 °C) resulted in improved performance. A non-monotonic trend in polarization resistance with increasing infiltration step count (V4.4a to V4.4c or V4.5a to V4.5c) was observed: while one additional infiltration step initially lowered polarization resistance, further infiltration led to a decline in performance. Structural analysis attributed this deterioration to the agglomeration of nanoscale Ni particles following repeated infiltration, which may have suppressed activation of the GDC surface. Cells from V4.4b presented a polarization resistance of $0.10\ \Omega\text{cm}^2$ at 550 °C, equal to one-sixth of that of V1.5a. This suggests a possible value under $0.10\ \Omega\text{cm}^2$ at 600 °C, making V4.4b likely the best-performing subvariant in this work.

Cells from V3.12 exhibited performance comparable to V1.5a, except for V3.12a. Among the three subvariants, the cells from V3.12c showed unstable initial performance. This could be partly attributed to insufficient GDC percolation.

4.2.2 Structural Analysis of Pristine Cells

Following the initial electrochemical characterization, selected cells were examined by SEM. These results were shared with the Forschungszentrum Jülich as part of a collaborative effort to optimize electrode performance. This section presents representative structural analyses aiming at identifying key factors that dominate cell performance.

Two SEM instruments were employed in this work. The first is the ZEISS 1540 XB-SEM (Carl Zeiss NTS GmbH) at IAM-ET, which provides excellent resolution of surface topography in SE mode. All SEM images acquired in SE mode were obtained using this instrument, with the electron beam oriented perpendicular to the sample cross-section (EHT = 1.30 kV).

To enhance the contrast between Ni and GDC phases, a Thermo Scientific™ Helios G4 FX DualBeam™ (Thermo Fisher Scientific, Waltham, MA, USA) at LEM was employed. The BSE images were captured using an ICD detector at 3.00 kV, with a beam current of 0.20 nA and a tilt angle of 52.0°.

Variants V2 and V5 served as process validation samples for the paste formulation and sintering protocol used for V1 and V3, respectively, and are therefore omitted from this study due to their similarity.

Variant V1 from Scree Printing of Usual Jülich Paste

A factor strongly influencing performance is sintering temperature. SEM images of polished cross sections (Figure 4.9) show Ni particle diameter of $0.5\ \mu\text{m}$ in cell IS1-446_V1.2b, and $0.35\ \mu\text{m}$ in IS1-474_V1.5a. The GDC particle size decreased from $0.5\ \mu\text{m}$ to $0.2\ \mu\text{m}$ when the sintering temperature was reduced from 1400 to $1200\ ^\circ\text{C}$. This leads to an increase in the density of TPB and DPB, which accounts for the superior performance of variant V1.5a ($0.29\ \Omega\text{cm}^2$ compared to $0.55\ \Omega\text{cm}^2$ for variant V1.2b).

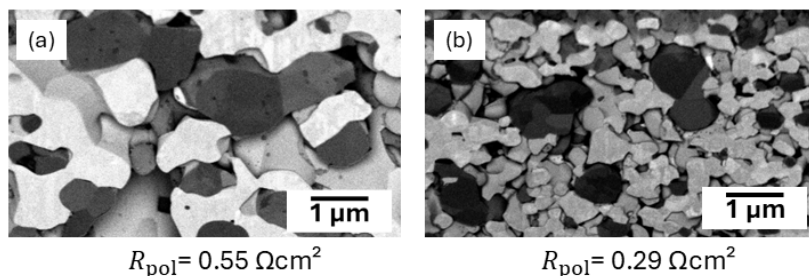


Figure 4.9: SEM/BSE images of polished cross sections of (a) cell IS1-446_V1.2b (sintering temperature $1400\ ^\circ\text{C}$) and (b) IS1-474_V1.5a (sintering temperature $1200\ ^\circ\text{C}$) after reduction at $650\ ^\circ\text{C}$. The lighter gray indicates GDC, and the darker gray indicates Ni. The polarization resistances were measured initially under nominal conditions. Adapted from (7).

The polarization resistance of variant V1.4 decreased from 0.78 to $0.51\ \Omega\text{cm}^2$ by applying a finer current collect layer, corresponding to a reduction of roughly 30%. Figure 4.10 shows that cell IS1-454_V1.4b, with relatively coarse Ni ($1.4\ \mu\text{m}$) in the current collect layer, exhibited approximately 30% lower coverage over the electrode surface compared to a finer contact layer ($0.5\ \mu\text{m}$), resulting in a smaller electrochemically active area and worse performance.

As shown in Figure 4.8, a drop of more than 50% in the polarization resistance was observed for variant V1.2 with decreasing reduction temperature. Comparing Figures 4.11(a) and (b), GDC particle size increased slightly, accompanied by Ni agglomeration (d_{Ni} from 0.6 to $0.8\ \mu\text{m}$, analyzed using ImageJ) at higher reduction temperature. Notably, Ni nanoparticles appeared on the GDC surface in samples reduced at $650\ ^\circ\text{C}$ (Figure 4.11(d)), acting as an electrocatalyst and enhancing electrochemical activity, similar to that observed with Ni infiltration. Cells reduced at

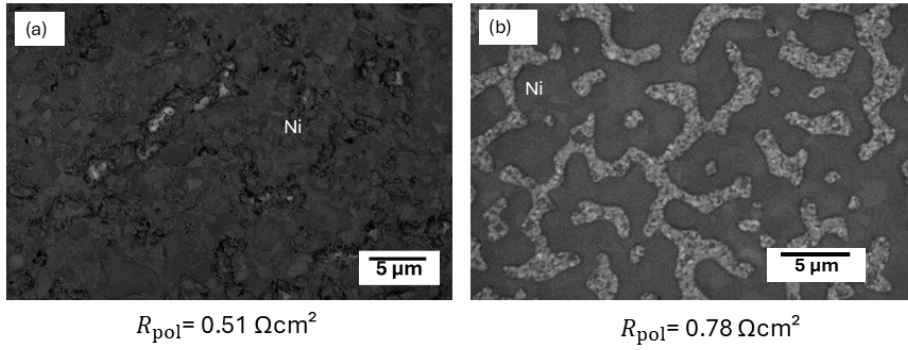


Figure 4.10: SEM images of the top view of the contact layer of (a) cell IS1-454_V1.4a, Ni particle size 0.5 μm , and (b) cell IS1-454_V1.4b, Ni particle size 1.4 μm . The polarization resistances were measured initially under nominal conditions. Darker gray denotes Ni, and lighter gray indicates GDC.

800 °C exhibited smooth GDC surfaces without these features. Similar differences were observed in other cells from V1 reduced at 800 and 650 °C.

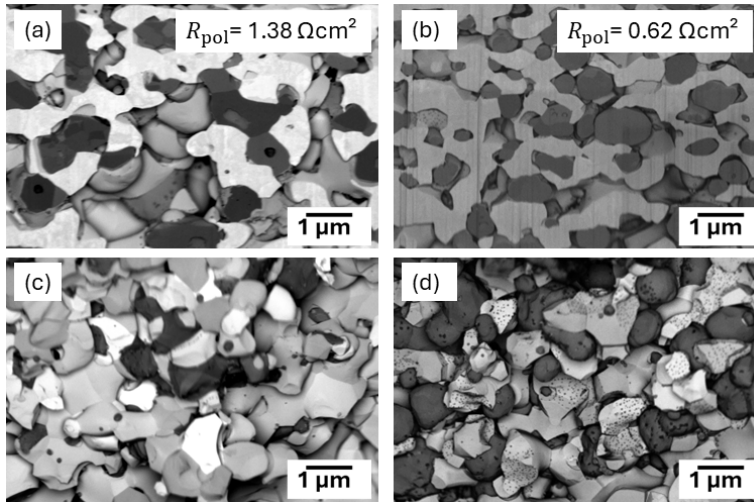


Figure 4.11: SEM/BSE images of polished cross sections of the electrode of cells reduced at (a) 800 (IS1-444_V1.2) and (b) 650 °C (IS1-442_V1.2). Fractured cross-sections are presented in (c) and (d). The lighter gray indicates GDC, and the darker gray indicates Ni. The polarization resistances were measured initially under nominal conditions. Figures (b, d) are adapted from (7).

Variant V3 from Screen Printing of a Fine Particle Paste

Several combinations of fine Ni and GDC particles were tested. Cell variants V3.1 to V3.11 exhibited poor performance, reproducibility, mechanical instability, and delamination, thereby disabling structural analysis.

SEM images of the V3.12a/b/c variants reduced at 650 °C are shown in Figure 4.12. These cells exhibited both excellent polarization resistance and good mechanical stability. Lower sintering temperatures resulted in smaller GDC particles, increasing TPB and DPB density. Interestingly, intermediate sintering temperatures yielded the best performance (IS1-465_V3.12b, sintered at 1,080 °C, $R_{pol} = 0.17 \Omega\text{cm}^2$), while cell IS1-464_V3.12c (sintered at 980 °C) showed slightly worse performance, likely due to insufficient GDC phase percolation, limiting ionic conductivity as shown in Figure 4.12(c).

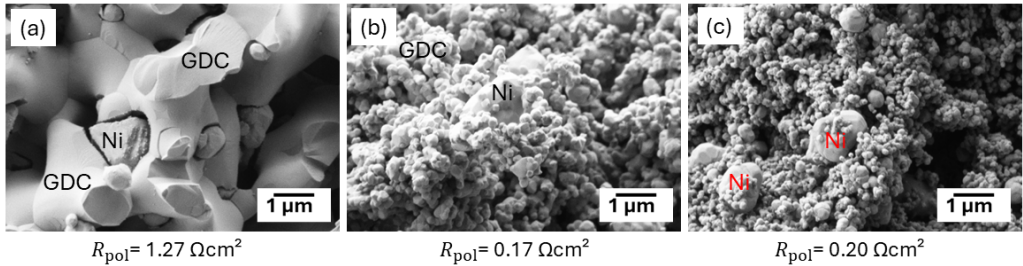


Figure 4.12: SEM/SE images of fractured cross sections of cell (a) IS1-466_V3.12a, sintered at 1400 °C, (b) IS1-465_V3.12b, sintered at 1080 °C, and (c) IS1-464_V3.12c, sintered at 980 °C. The polarization resistances were measured initially under nominal conditions. Adapted from (7).

Variant V4 from Infiltration of Ni into a GDC Skeleton

Due to the limited number of available samples, the analysis was confined to three V4.4 cells aged at 500 °C for 100 h and one pristine cell, IS1-462_V4.5b, as shown in Figure 4.13. All samples were reduced at 550 °C. Consequently, a direct quantitative comparison of polarization resistance relating to the electrode structure is not possible. The discussion therefore focuses on qualitative microstructural observations and their potential implications for cell performance.

An increasing number of infiltration steps leads to a gradual increase in the size of Ni particles. Cell IS1-450_V4.4a exhibited Ni particles smaller than 10 nm, while cell IS1-449_V4.4b showed particle sizes below 25 nm. In cell IS1-449_V4.4c, Ni particles with sizes below 50 nm were observed. All three cells exhibited a comparable GDC particle size of approximately 0.35 μm.

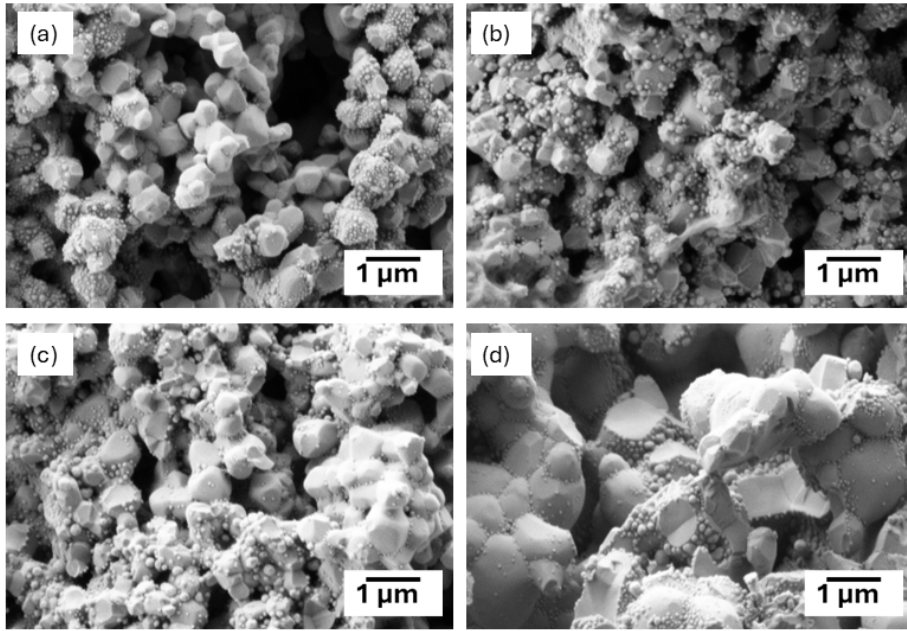


Figure 4.13: SEM/SE images of fractured cross sections of cells (a) IS1-450_V4.4a, infiltrated once, (b) IS1-449_V4.4b, infiltrated twice, and (c) IS1-449_V4.4c, infiltrated three times, all sintered at 1200 °C, and (d) cell IS1-462_V4.5b, infiltrated twice, sintered at 1300 °C. Larger particles are GDC, whereas finer particles are Ni. Adapted from (7).

For cell IS1-449_V4.4c, a saturation of the infiltration may have been reached. This is supported by the presence of visible Ni agglomeration, which is likely responsible for the slight reduction in electrochemical performance.

In contrast, the pristine cell IS1-462_V4.5b exhibited significantly larger GDC particles and a lower DPB density. These features can be attributed to the higher sintering temperature applied during fabrication and are consistent with the inferior performance compared to the V4.4 variants.

Variant V6 from Infiltration of GDC into a Ni Skeleton

The results presented in this section have been published in (6).

To study the degradation behavior of the fine GDC phase, most V6 cells were operated at elevated temperatures after initial characterization, which limited the available SEM analysis. Figure 4.14(a) and (b) present polished and unpolished cross sections of cell IS1-438_V6.5 reduced at 650 °C, revealing the microstructural features underlying the superior performance.

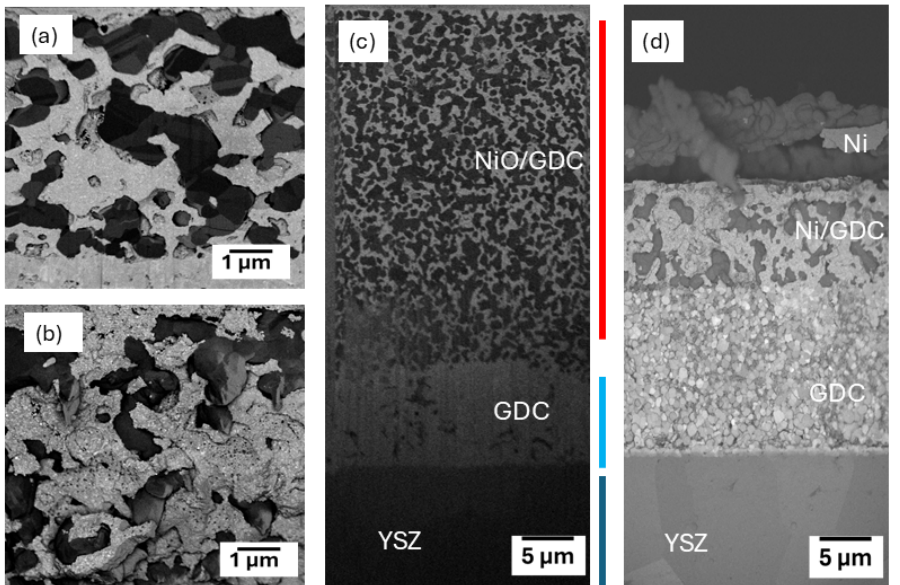


Figure 4.14: SEM/BSE images of (a) polished and (b) fractured cross sections of the electrode of cell IS1-438_V6.5, after reduction at 650 °C. SEM/BSE of a polished cross-section of (c) unreduced cell V6.11 and (d) reduced cell IS1-438_V6.5. In all the Ni(NiO)/GDC, the lighter gray denotes GDC and the darker gray Ni/NiO. Adapted from (6).

The electrode of IS1-438_V6.5 exhibits a coarse Ni framework that provides mechanical stability, while fine GDC particles occupy the pores, accounting for 37 vol.%. Overall porosity of V6 is 23 vol.%, roughly 10 vol.% lower than in screen-printed cells. Small pores form around Ni particles (Figure 4.14(a)), likely resulting from NiO reduction and shrinkage. The fine GDC phase generates a large DPB in addition to the TPB surrounding Ni particles (Figure 4.14(b)).

A thick GDC interlayer ($>10\text{ }\mu\text{m}$) and an additional thin GDC layer between Ni/GDC and the Ni contact layer were consistently observed (Figure 4.14(d)). To investigate the origin of this feature, SEM analysis was performed on an unreduced cell from V6.11. As the sintering temperature and infiltration conditions were similar, a qualitative comparison between the unreduced cell from V6.11 and the reduced cell IS1-438_V6.5 is considered reasonable.

Figure 4.14(c) shows that the unreduced NiO/GDC electrode initially was $30\text{ }\mu\text{m}$, decreasing to $5\text{ }\mu\text{m}$ after reduction. In contrast, the GDC interlayer thickened from 5 to $9\text{ }\mu\text{m}$, and a thin GDC layer ($1\text{ }\mu\text{m}$) formed atop the Ni/GDC layer. These observations indicate potential electrode reorganization during reduction, with reduced Ni particles moving towards the electrode center, leaving the top and bottom of the electrode Ni-free. This resulted in interlayer expansion and the

formation of a new GDC layer beneath the contact layer, both contributing to a slight increase in the cell's ohmic resistance.

Summary

The infiltration of Ni into the GDC scaffold appears to be the most promising approach to improve electrode performance, followed by infiltration of GDC into a Ni scaffold. The enhanced performance in the former case is likely related to the fine Ni particles, which may improve electrochemical activity at the GDC surface. In contrast, in the latter case, the increased GDC surface area and higher TPB density associated with smaller GDC particle sizes appear to be the dominant contributing factors.

The use of ultra-fine particles in the screen-printing paste was also effective, likely due to the resulting finer GDC microstructure. In contrast, screen printing with the usual Jülich paste resulted in the highest polarization resistance.

Among the fabrication parameters, lowering the sintering temperature (above 1000 °C) had a significant positive impact on electrode performance, as it generally leads to a finer electrode microstructure. The number of infiltration steps had only a minor effect on both infiltrated cell types, possibly due to saturation effects.

For the screen-printed cells, the presence of an interlayer appeared to enhance electrode performance, potentially by improving adhesion between the electrode and electrolyte. A finer contact layer is preferred, as structural analysis revealed that the Ni/GDC electrode was not fully covered with the coarser contact layer, resulting in a partially activated electrode.

This section presented the initial characterization, showing that lower sintering temperatures, finer particle sizes in the paste, and optimized infiltration processes were associated with improved electrode performance. Although the presence of an interlayer and a contact layer with smaller Ni particles also contributed, their effects were comparatively less pronounced. An important factor after fabrication was the reduction protocol, where milder reducing conditions, such as 650 °C, led to improved electrode performance.

In total, 11 subvariants achieved the target polarization resistance of $R_{\text{pol}} \leq 0.25 \Omega\text{cm}^2$ (reported in (276)) under nominal operating conditions. However, this sample pool was considered too small, as a significant number of samples were expected to be excluded during subsequent characterization for electrode process identification and durability testing under elevated stress conditions. To ensure a sufficiently large set of candidates for further investigation, the selection criterion for the initial filter was relaxed to $R_{\text{pol}} \leq 0.80 \Omega\text{cm}^2$. This threshold was chosen based on reported performance levels of commercial cells (86).

Considering both electrochemical performance and mechanical stability, cells from V1, V3.12, V4.4, V4.5, and V6 were selected as the most promising candidates. These samples, reduced at 650 °C or lower, form the basis for subsequent investigations into degradation behavior and the development of an aging model.

4.3 Electrochemical Characterization of Selected Ni/GDC Anodes

As discussed in Section 2.3, various loss mechanisms occur across cell components, including the anode, cathode, electrolyte, interlayer, and gas diffusion layer. Since this work focuses on modeling the aging of the Ni/GDC electrode, it is critical to primarily isolate losses attributable to it. For this purpose, a systematic characterization involving variations in multiple operating parameters was performed. EIS measurements were conducted under conditions in line with those reported in (196, 238). All tests were recorded at OCV with a total gas flow rate of 0.500 slm. Very low vapor and hydrogen partial pressures were avoided to prevent electrode starvation while maintaining a reducing atmosphere.

To minimize changes in cell state during parameter variations, sensitivity tests were conducted either at temperatures below the reduction temperature or after mid- to long-term operation at elevated temperatures until the polarization resistance reached a steady state.

Similar impedance behavior was observed among subvariants of the same variant. Therefore, one representative example with the most pronounced features and dependencies was selected for each variant. For clarity, the sensitivity test results are first presented for the V6 cells, which exhibited the most distinct and separable impedance features. The cell IS1-669_V1.5a was chosen as representative of the V1 variant, as two distinct mid-frequency processes are visible. Finally, a brief discussion of the fine-structured cells from V3.12 and V4 is provided.

4.3.1 Variant V6 from GDC Infiltrated into a Ni Skeleton

All the cells discussed in this section are subvariants V6.1 and V6.5 of variant V6, which incorporates thick GDC interlayers and electrodes prepared by infiltrating GDC into a NiO skeleton sintered at 1,100 °C. The two subvariants differ in the number of infiltration steps, with V6.1 and V6.5 undergoing nine and five infiltration steps, respectively. Initial electrochemical characterization and structural analyses confirmed the similarity between the two subvariants. Although these cells (including those of subvariant V6.8, which underwent ten infiltration steps)

differ in the number of infiltration cycles, their electrode microstructures and aging characteristics are sufficiently similar to allow quantitative comparison within the scope of this work.

The results presented in this section were previously reported in (6).

Figure 4.15 shows the DRTs of measured impedance spectra for the electrode of cell IS1-437_V6.1, at temperatures between 845 and 900 °C under varying gas compositions, as well as for the cell IS1-441_V6.5, at 700 °C with alternating inert gas. These tests were performed on the former cell after operation at 900 °C for 650 hours, while the inert gas variation test was conducted on the latter after operation at 700 °C for 900 hours.

Compared to the two main loss processes reported in (196, 238), additional processes with non-negligible contributions were visible. At 845 °C, four visible peaks, LF_1 , LF_2 , MF_1 , and MF_2 from low to high frequency, can be distinguished. At higher temperatures and/or lower steam content, the process observed between 30–1000 Hz at 600 °C with 50% humidity in hydrogen appears to separate into two middle-frequency processes, MF_1 and MF_2 . Based on (196), high-frequency processes ($HF > 10,000$ Hz at 845 °C) correspond to resistances accounting for the electrolyte and the GDC/YSZ interface and are therefore not discussed further.

Figure 4.15(a) shows that all processes except LF_1 are thermally activated and can be attributed to charge transport and/or charge transfer processes. The weak temperature dependence of LF_1 suggests a possible association with gas diffusion. The second middle-frequency process reported in (196) is not comparable to MF_2 observed in our cells regarding either temperature dependence or magnitude. Therefore, MF_2 is likely significant, and understanding its origin could be important.

To investigate the influence of fuel humidification, the steam content was varied between 0.05 and 0.50 atm with a constant hydrogen partial pressure of 0.3 atm at 845 °C. A relatively high temperature was chosen to minimize overlap between MF_1 and MF_2 . Figure 4.15(b) shows that LF_1 exhibits the strongest dependence on steam content, followed by LF_2 , with increasing steam significantly reducing their contributions to polarization resistance. MF_1 displays a weaker dependency, consistent with (196), and can be attributed to oxygen ion transport in the GDC phase. The higher oxygen partial pressure resulting from increased steam may partly reduce GDC ionic conductivity, explaining the slight increase in MF_1 . MF_2 shows negligible dependency on steam partial pressure.

Compared to steam variations, all processes exhibit weaker dependency on hydrogen partial pressure (Figure 4.15(c)). Among them, LF_1 is most sensitive, followed by LF_2 , both showing decreasing contributions to polarization resistance with increasing hydrogen partial pressure. The peaks shift towards lower frequencies, indicating an increase in chemical capacitance. MF_1 exhibits a weak dependency, likely due to GDC ionic and electronic conductivity being influenced

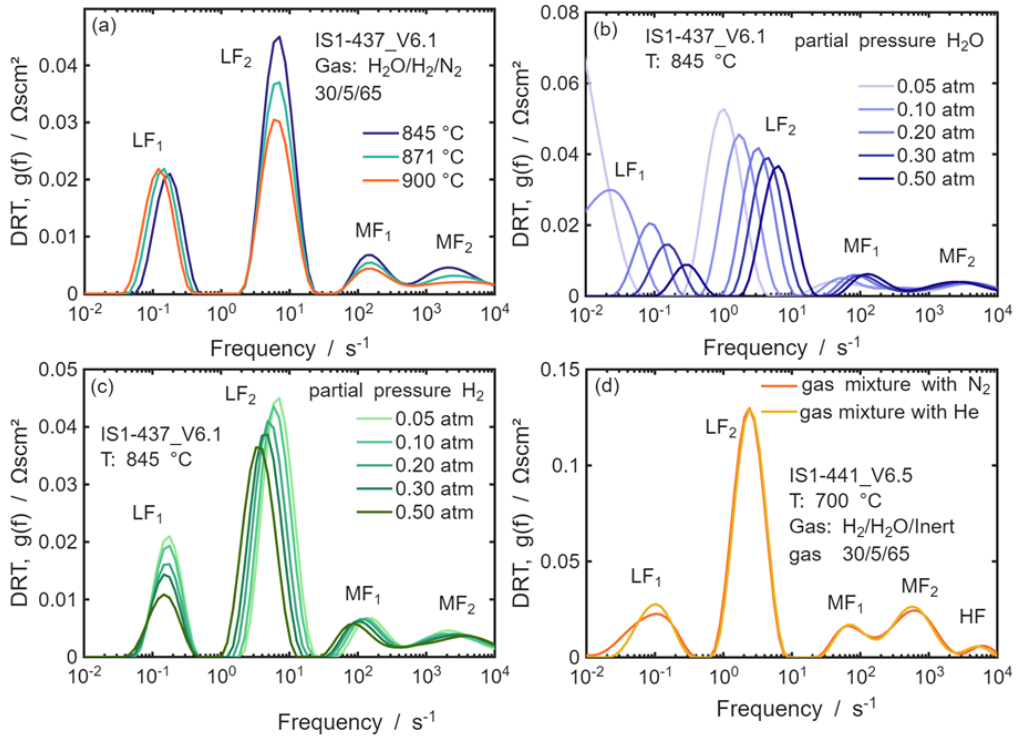


Figure 4.15: DRTs of the impedance spectra of the electrode of cell IS1-437_V6.1, (a) at different temperatures between 845 °C and 900 °C with steam and hydrogen partial pressures of 0.05 and 0.30 atm, respectively, using nitrogen as the inert gas, (b) at 845 °C when varying the steam partial pressure from 0.05 to 0.50 atm while keeping the hydrogen partial pressure constant at 0.30 atm with nitrogen as the inert gas, (c) at 845 °C when varying the hydrogen partial pressure from 0.05 to 0.50 atm while keeping the steam partial pressure constant at 0.30 atm with nitrogen as the inert gas. (d) DRTs of the impedance spectra of the electrode of cell IS1-441_V6.5, under different inert gases at 700 °C with steam and hydrogen partial pressures of 0.05 and 0.30 atm, respectively. Adapted and modified from (6).

by oxygen partial pressure. MF_2 remains nearly unaffected. Due to its small magnitude and strong peak overlap, a precise description of its behavior is not feasible.

An inert gas variation test on cell IS1-441_V6.5, analogous to the procedure in (238), was conducted. Figure 4.15(d) shows that LF_1 clearly depends on the inert gas, producing a $5.00 \text{ m}\Omega \text{cm}^2$ difference in polarization resistance. This value is nearly three times smaller than that reported in (238) for a general single-cell test setup at IAM-ET, KIT. This decrease is likely due to lower testing temperature, different gas compositions, and the application of the active-driven gas layer concept. The low frequency of LF_1 (0.1 Hz at 845 °C) may result from geometry differences. LF_2 and MF_1 remain unaffected, indicating no relationship to gas diffusion. The small variation

observed for MF_2 ($0.50 \text{ m}\Omega\text{cm}^2$) is likely within measurement error, while it is only 10% of the resistance difference induced by exchanging inert gas.

Based on these observations, LF_1 , LF_2 , and MF_1 are associated with gas diffusion, surface, and bulk processes, respectively, consistent with (196). The origin of MF_2 remains unassigned. At 600°C , where reference impedances were measured, MF_1 and MF_2 are not separable. Thus, electrode degradation analysis probably relies on the evolution of LF_2 .

4.3.2 Variant V1 from Screen Printing of Usual Jülich Paste

The cells discussed in this section are subvariants V1.4a and V1.5a of variant V1, fabricated by screen printing using the usual Jülich paste. Both variants are without a GDC interlayer. Their electrodes were sintered at $1,300$ and $1,200^\circ\text{C}$, respectively, with a contact-layer particle size of $0.5 \mu\text{m}$.

Compared with variant V6, V1 cells exhibit a less pronounced gas-diffusion peak and a greater overlap between the two mid-frequency peaks. For example, cell IS1-469_V1.5a, reduced at 650°C and aged at 700°C for 550 h, shows four visible peaks at 700°C , LF_2 , MF_1 , MF_2 and HF (Figure 4.16). At lower steam/hydrogen contents, the process between 1000 and 10,000 Hz separates into MF_1 and MF_2 . Figure 4.16(a) demonstrates that LF_2 , MF, and HF are thermally activated, similar to that observed in Figure 4.15(a). Steam variation (Figure 4.16(b)) shows that LF_2 and MF_1 contributions decrease with increasing steam content, while MF_2 and HF remain largely unaffected. The impact of hydrogen partial pressure on the three visible peaks, presented in Figure 4.16(c), is comparable to that of cell IS1-437_V6.1 in Figure 4.15(c), except for a weaker dependency.

However, the contribution of the HF process to the overall resistance within the measured frequency range is significantly larger than that observed in other cells fabricated using the same paste recipe but sintered at different temperatures. This difference may be attributed to variations in sintering temperature and fabrication sequence, as the V1.5a cells were produced last, and the paste may have partially dried before use. Despite this, the V1.5a cells exhibited excellent reproducibility and consistent performance within the same batch. Furthermore, since the HF peak does not overlap with other relevant processes, it can be excluded from further analysis.

Due to a gas line interruption, the alternating inert gas test could not be performed on the same V1.5a cell. Instead, the results from cell IS1-454_V1.4a at 700°C after 900 h are used as an approximation, as shown in Figure 4.16(d). An $8.00 \text{ m}\Omega\text{cm}^2$ reduction in polarization resistance was observed. The cell exhibited an LF_1 peak that did not overlap with the LF_2 peak, which decreased significantly when the inert gas was switched from nitrogen to helium. A similar

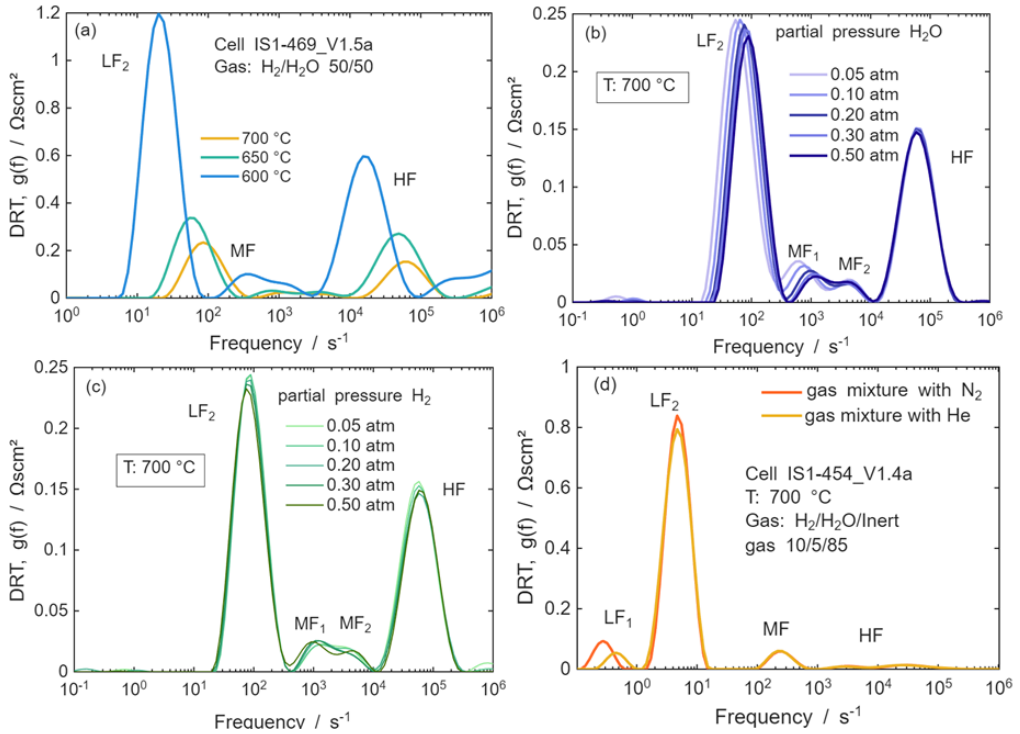


Figure 4.16: DRTs of the impedance spectra of the electrode of cell IS1-469_V1.5a: (a) at different temperatures between 600 and 700 °C, (b) at 700 °C when varying the steam partial pressure from 0.05 to 0.50 atm while keeping the hydrogen partial pressure constant at 0.30 atm with nitrogen as the inert gas, (c) at 700 °C when varying the hydrogen partial pressure from 0.05 to 0.50 atm while keeping the steam partial pressure constant at 0.30 atm with nitrogen as the inert gas. (d) DRTs of the impedance spectra of the electrode of cell IS1-454_V1.4a under different inert gases at 700 °C with steam and hydrogen partial pressures of 0.05 and 0.10 atm, respectively. Adapted from (7).

but smaller decrease was observed for LF_2 . After applying a CNLS fit with an RQ element representing LF_2 , the change in its resistance was determined to be $2.00 \text{ m}\Omega\text{cm}^2$, representing 25% of the total resistance change. This suggests that part of the LF_2 response may also be associated with gas diffusion effects, indicating an overlap between gas diffusion and surface-related electrochemical processes in this frequency range. By analogy, the LF_2 peak of cell IS1-469_V1.5a is likely an overlap of these two processes. Since these two cells have a similar electrode thickness ($8 \text{ }\mu\text{m}$), which is more than one order of magnitude smaller than the Ni mesh thickness ($200 \text{ }\mu\text{m}$), the gas diffusion loss is primarily located in the interfacial space in the mesh. Therefore, the calculated gas diffusion resistance for cell IS1-454_V1.4a is considered representative also for IS1-469_V1.5a.

The calculated value based on the method described in (238) and Equations 2.20 to 2.24 under nominal operating conditions is $2.50 \text{ m}\Omega\text{cm}^2$, accounting for less than 1% of the total polarization resistance of the V1 cell variant. For CNLS fitting, the precision of the fitted R_{LF_2} can be improved by applying the RQ elements and subtracting this value from the fit results. When using a transmission line model, the precision of the fitted r_{ct} can be preserved by introducing an RQ element with a fixed resistance value in the low-frequency range.

In summary, the identification of electrode processes in variant V1.5a is complete. The results are largely consistent with those observed in V6 cells, with the exception that gas diffusion and charge-transfer processes appear to overlap in the impedance spectrum.

4.3.3 Variants with Fine Electrode Structure

The cells discussed in this section are the subvariants V3.12b from V3.12, as well as V4.4b and V4.5b from V4.4 and V4.5, respectively. Subvariant V3.12b was fabricated via screen printing of a fine particle paste, followed by sintering at 1080°C . Subvariant V4.4b was produced by double infiltration of Ni into a GDC scaffold sintered at 1200°C . Subvariant V4.5b was prepared analogously, with the exception that the GDC scaffold was sintered at 1300°C .

Cell IS1-479_V3.12b was reduced at 550°C and operated at nominal conditions for 1000 h. A comparison of its impedance and the corresponding DRT before and after operation is shown in Figure 4.17(a, c). Although the impedance still exhibits the two-arc feature, it differs significantly from variants V1.5a and V6. The low-frequency process occurs around 600 Hz at 600°C , presenting a shift to higher frequencies and a much smaller contribution. High-frequency processes appear more dominant in this cell type, complicating CNLS fitting by gaining more weight, even though they are not the primary focus of this study.

Another issue is that aging increases peak overlap in the DRT spectrum. Notably, the peak initially located between 1000–10,000 Hz becomes indistinguishable after 1000 h. Moreover, the high-frequency processes degrade more rapidly than the low-frequency ones. In conclusion, variant V3.12b may not be suitable for developing an aging model, as reliable process identification within the electrode is hindered.

Cell variant V4.4b, fabricated via infiltration, exhibited similar behavior: charge-transfer processes contributed only a small fraction of the total impedance, and more pronounced degradation was observed at high frequencies. Consequently, a precise evaluation of the charge-transfer process is not feasible.

In contrast, cell IS1-458_V4.5b displayed more defined peaks in its DRT, similar to those of the V1.5a cells, with dominant LF_2 and high-frequency processes, as shown in Figure 4.17(b, d).

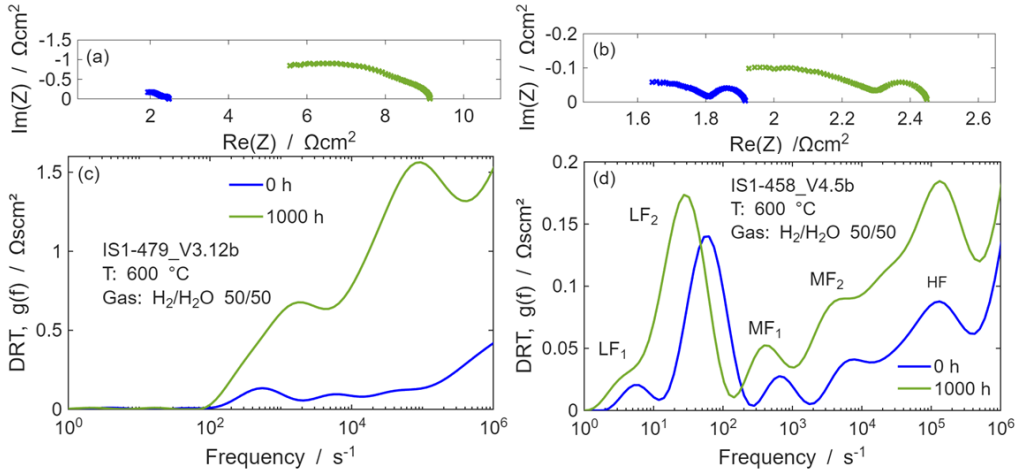


Figure 4.17: (a) Impedances and (c) corresponding DRTs of the cell IS1-479_V3.12b before and after operation at 600 °C for 1000 h. (b) Impedances and (d) corresponding DRTs of the cell IS1-458_V4.5b before and after operation at 600 °C for 1000 h. Adapted from (7).

However, due to the very fine Ni structure and its tendency to agglomerate under high temperature and humidity, sensitivity tests should be conducted at lower temperatures to preserve the Ni phase structure. Nevertheless, mid-term operation at 600 °C revealed continuous degradation, particularly in processes above 10,000 Hz, thereby increasing the overlap between MF_2 and HF processes. Since sensitivity tests are only reliable once the cell performance has stabilized, a condition not achievable within the project's time frame, variant V4.5b was not considered further.

Summary

A detailed investigation on the V1 and V6 cells enabled the identification of two low-frequency processes (LF_1 and LF_2) and one middle-frequency process (MF_1), attributed to gas diffusion, surface reactions, and bulk processes, respectively. An additional middle-frequency process (MF_2) was observed, but its origin could not be clearly identified.

An equivalent circuit model for CNLS fitting, shown in Figure 4.18, was established for one electrode of the cell. It consists of an ohmic resistance Z_{YSZ} , a transmission line model describing coupled electrode processes LF_2 and MF_1 , and three $\text{R}||\text{CPE}$ elements representing an unassigned middle-frequency process (MF_2), the high-frequency process (HF), and the gas-diffusion-related process (LF_1), respectively. The LF_1 element includes a fixed resistance value determined from Equations 2.20–2.24, 2.31.

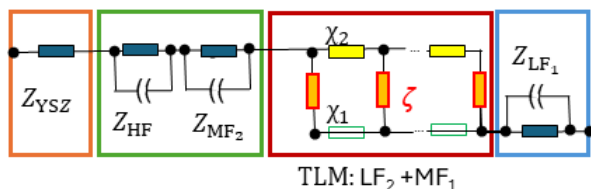


Figure 4.18: Equivalent circuit model for cell variants V1 and V6. Adapted from (7).

Variants V4.4a and V3.12b exhibited dominant, overlapping high-frequency processes, which did not allow robust CNLS parameter extraction for detailed evaluation. Although variant V4.5b exhibited impedance characteristics similar to those of variants V1.5a and V6, sensitivity tests following long-term operation could not be performed due to project time constraints.

Given the focus of this work on developing a methodology for electrode aging modeling, only cells from V1 and V6 with identifiable electrode loss processes were selected for operation under varied conditions to establish a suitable protocol for accelerated stress testing.

4.4 Accelerated Durability Tests at Elevated Stressors

Designing an appropriate test protocol is essential for reliably predicting the aging behavior of electrodes, particularly because large deviations are often reported between measured and estimated lifetimes (296). Lifetime prediction is typically performed by extrapolating degradation-time distributions obtained under accelerated conditions to nominal stressors (19, 20, 21, 22). However, this approach is generally valid when the dominant aging mechanisms under accelerated and nominal conditions are comparable.

In a full cell, multiple degradation mechanisms can simultaneously influence performance, with their relative contributions depending on operating temperature, gas composition, load, and time. Consequently, empirical statistical models are typically applicable within narrow time frames or under specific stress conditions in which a single aging mechanism dominates (208). If the dominant mechanism changes, for instance between 600 °C and 900 °C, extrapolation from high- to low-temperature conditions may lead to significant prediction errors.

To address this challenge, several symmetrical cells from V1 and V6 were operated over a temperature range of 600–900 °C and relative humidity levels of 10–50% to investigate aging behavior. The cell type, test number, gas atmosphere, operating temperature, duration, and corresponding section of this work are summarized in Table 4.3.

Table 4.3: Summary of cells tested under nominal and elevated operating conditions. Cells No. 1–10 were fabricated via screen printing using the usual Jülich paste (see Table A.3). Cells No. 11–24 were produced by infiltrating fine GDC into a Ni scaffold (see Table A.6).

No.	Cell ID	Reduction T (°C)	T_{age} (°C)	Humidity (%)	Time (h)	Section
1	IS1-424_V1.2_1	800	900	50	250	4.4.1.1.1
2	IS1-429_V1.2_1	800	900	50	1100	4.4.1.1.1
3	IS1-470_V1.5a	650	900	50	130	4.4.1.1.2
4	IS1-443_Ref1	650	800	50	953	4.4.1.2.1
5	IS1-443_V1.2	650	800	50	953	4.4.1.2.2
6	IS1-445_V1.2	650	800	10	390	4.4.1.2.3
7	IS1-456_V1.2	650	750	50	180	4.4.1.3
8	IS1-456_V1.2b	650	750	50	180	4.4.1.3
9	IS1-456_V1.2c	650	750	50	180	4.4.1.3
10	IS1-448_V1.2b_2	650	600	50	550	4.4.1.3
11	IS1-430_V6.1	800	900	50	830	4.4.2.2
12	IS1-430_V6.2	800	900	50	830	4.4.2.2
13	IS1-430_V6.3	800	900	50	830	4.4.2.2
14	IS1-437_V6.1	650	900	50	650	4.4.2.1
15	IS1-437_V6.3	650	900	50	650	4.4.2.2
16	IS1-443_V6.11_1	650	800	50	953	4.4.2.2
17	IS1-443_V6.11_2	650	800	50	953	4.4.2.2
18	IS1-443_V6.11_3	650	800	50	953	4.4.2.2
19	IS1-445_V6.11_1	650	800	10	390	4.4.2.2
20	IS1-445_V6.11_2	650	800	10	390	4.4.2.2
21	IS1-441_V6.4	650	700	50	1050	4.4.2.2
22	IS1-441_V6.5	650	700	50	1050	4.4.2.1
23	IS1-441_V6.6	650	700	50	1050	4.4.2.2
24	IS1-441_V6.7	650	700	50	1050	4.4.2.2

In this table, cells No. 1–10 correspond to screen-printed cells fabricated using the usual Jülich paste. Most belong to variant V1, with the exception of Ref1, which consists of a single GDC layer sintered at 1300 °C. Among these cells, only subvariant V1.2 includes a GDC interlayer sintered at 1300 °C, while its electrode was sintered at 1400 °C. The remaining cells were fabricated without an interlayer and differ in electrode sintering temperature (1400 °C for V1.2b and 1200 °C for V1.5a) as well as in the particle size of the contact layer (0.5 μm for V1.2b and V1.5a, and larger particles for V1.2c). A detailed description of the cell variants is provided in Table A.3.

Cells No. 11–24 were fabricated by infiltrating GDC into a Ni scaffold. These cells differ in sintering temperature, infiltration concentration, and the number of infiltration steps, as summarized in Table A.6. Subvariants V6.1–V6.3 were sintered at 1100, 1200, and 1300 °C, respectively, and each underwent nine infiltration cycles using a saturated $\text{GDC}(\text{NO}_3)_2$ solution. Subvariants V6.5–V6.7 and V6.8–V6.10 are analogous to V6.1–V6.3 but differ in the number of infiltration cycles, with five and ten cycles, respectively. V6.4 differs from V6.5 only in its lower sintering temperature of 1025 °C. Subvariant V6.11 was fabricated by infiltrating a 3 mol/L $\text{GDC}(\text{NO}_3)_2$ solution 15 times into a Ni scaffold sintered at 1100 °C.

Within each variant group (i.e., cells No. 1–10 and No. 11–24), comparable cells were aged under different operating conditions to investigate the influence of these conditions on degradation behavior. In addition, comparisons both within and between the two groups enable the evaluation of aging behavior across different cell (sub-)variants under similar operating conditions.

The aim is to identify regimes where different aging mechanisms dominate and to evaluate whether extrapolation between them is scientifically justified. Structural analysis combined with electrochemical testing can help determine whether the observed degradation behavior is consistent with mechanisms occurring under nominal operating conditions.

In this section, the test results are first presented for V1 cells, then for V6, in order of decreasing temperature and humidity. Microstructural degradation was analyzed using EDS, SEM, and STEM. Based on these observations, the cell type most suitable for modeling and the optimal conditions for the AST protocol were determined.

4.4.1 Screen-Printed Cell Variant V1

4.4.1.1 Durability at 900 °C

4.4.1.1.1 Cells from V1.2 Operated at 50% Humidity in Fuel The cells from V1.2 investigated in this section consist of an electrolyte, two GDC interlayers sintered at 1300 °C, two Ni/GDC layers from the usual Jülich paste sintered at 1400 °C, and two Ni contact layers with a particle size of 0.5 μm . The results presented in this section are reported in (4).

To obtain an initial understanding of the aging behavior of screen-printed cells under accelerated conditions, two cells (IS1-424_V1.2_1 and IS1-424_V1.2_2) from V1.2 were integrated into a multi-cell test setup, with two additional cells positioned at the bottom and top of the assembly. These cells were reduced at 800 °C. Following initial characterization, the assembly was heated in a nitrogen: hydrogen mixture (90:10) to 900 °C and operated for 250 h after the gas atmosphere was adjusted to 50% H_2 + 50% H_2O . Contrary to the expected rapid degradation, all cells

exhibited a significant decrease in polarization resistance, as shown in Figure 4.19, with cell IS1-424_V1.2_1 (cell 2) chosen as a representative example.

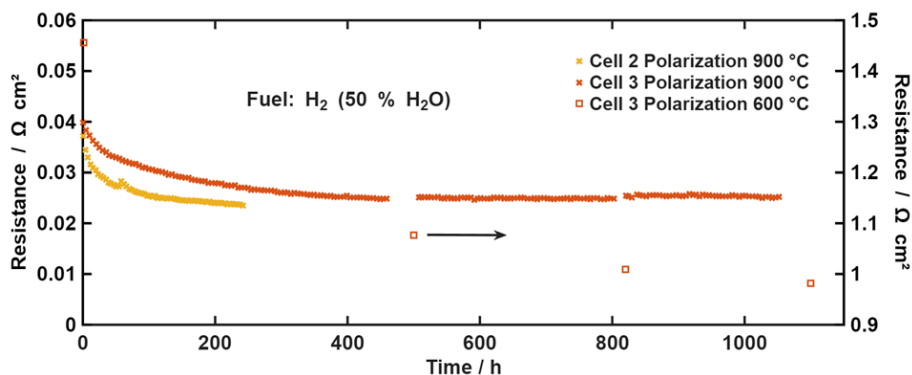


Figure 4.19: Time evolution of polarization resistances measured at 900 °C in a 1:1 H₂/H₂O mixture for Cell 2 (IS1-424_V1.2_1) and Cell 3 (IS1-429_V1.2_1), plotted on the left axis. Polarization resistance from the reference measurement of Cell 3 (IS1-429_V1.2_1) at 600 °C, under the same gas composition, is shown on the right-hand axis. All values are divided by 2 to represent single-electrode contributions. Adapted from (4).

To investigate the long-term behavior, another three cells (IS1-429_V1.2_1 to IS1-429_V1.2_3) from V1.2 were assembled for a repeat test. After identical reduction and characterization, the cells were again heated to 900 °C and operated for 1,100 h. During this test, reference measurements at 600 °C were conducted under the same gas composition. For a complete comparison, a separate set of three cells (IS1-427_V1.2_1 to IS1-427_V1.2_3) from V1.2 were demounted immediately after reduction and characterization.

A standard workflow to assess cell reproducibility starts with comparing the initial polarization resistance, whose deviations should be within 10%. The high reproducibility of the cells from V1.2 is shown in Figure 4.6(c). The next step is to compare the Nyquist plots and the corresponding DRT spectra. If the curves show good agreement, particularly in the low-frequency region, where electrode-related electrochemical reactions in the Ni/GDC electrode predominantly occur, the electrode structures can be assumed to be comparable. Consequently, any differences observed after the operation can be attributed to the operating conditions. For cells operated under identical conditions, the evolution of polarization resistance can then be compared (step 3). If they exhibit a similar aging trend, they can be considered to have excellent reproducibility. This behavior was observed for the cells tested in IS1-424 and IS1-429. For clarity and brevity, this three-step workflow is illustrated in detail using three representative cells from tests IS1-424, IS1-427, and IS1-429. The cell subjected only to reduction is referred to as cell 1 (IS1-427_V1.2_1),

while the cells aged for 250 h and 1100 h are denoted as cell 2 (IS1-424_V1.2_1) and cell 3 (IS1-429_V1.2_1), respectively.

The three cells initially exhibited polarization resistances of 0.077, 0.093, and 0.089 Ωcm^2 per electrode (800 °C, 50% H_2 + 50% H_2O). Differences are observed in the LF_1 peak below 1 Hz and minor variations in the LF_2 around 3 Hz, whereas higher-frequency responses show good agreement. As these features are related to electrochemical reactions and transport processes in the electrode, their correspondence indicates good microstructural reproducibility. Thus, the observed microstructural differences after testing are most likely attributable to high-temperature and humidity-induced structural and material changes.

The quantitative changes in polarization resistance for Cells 2 and 3 at 900 °C are summarized in Figure 4.19. The time intervals between approximately 500–535 h and around 820 h correspond to an interruption of the oxygen supply and a reference measurement at 600 °C, respectively. The difference in polarization resistance between the two cells remains within 10%, indicating good reproducibility. The polarization resistance decreases significantly during the first 200 h of operation, followed by a milder decline, reaching a stable value after approximately 650 h.

The observed improvement can be attributed to complex structural and/or material changes within the electrode layer. From the DRTs shown in Figure 4.20(b), the enhancement primarily occurs in the peak between 1–30 Hz, which corresponds to overlapping contributions from gas diffusion and the charge transfer reaction. A similar decrease in R_{Poi} was reported during the initial operation phase of anode-supported cells with a Ni/YSZ cermet anode and substrate (297), which, according to DRT analysis, could be related to improved gas diffusion in the anode substrate.

In the present study, R_{Poi} decreased to 60% of its initial value within 650 h at 900 °C. This improvement cannot be solely attributed to enhanced gas diffusion resistance, as it is also evident in the reference measurements carried out at 600 °C, as presented in Figure 4.21. Specifically, R_{Poi} at 600 °C decreases by 0.47 Ωcm^2 after 1100 h of operation. This value is roughly ten times larger than the total estimated polarization loss of 4.50 $\text{m}\Omega\text{cm}^2$ at 900 °C. Therefore, the change cannot be attributed to the nearly temperature-independent gas diffusion resistance.

Based on the relationship between material, structure, and performance presented in (239), the lowering of LF_2 and its shift toward higher frequencies must be attributed to a decrease in the r_{ct} , reflecting an increase in electrocatalytic activity and/or the density of active reaction sites. For the MIEC GDC phase, this increase is not limited to the continuous Ni matrix but also extends to TPBs of isolated Ni particles on the GDC surface, as well as the GDC surface itself. The samples were further investigated using EDS, FIB/SEM, and STEM in post-test analysis.

One possible explanation for the observed performance improvement is Ni transport into the porous GDC interlayer underneath the Ni/GDC anode, similar to the variant Ref1 presented

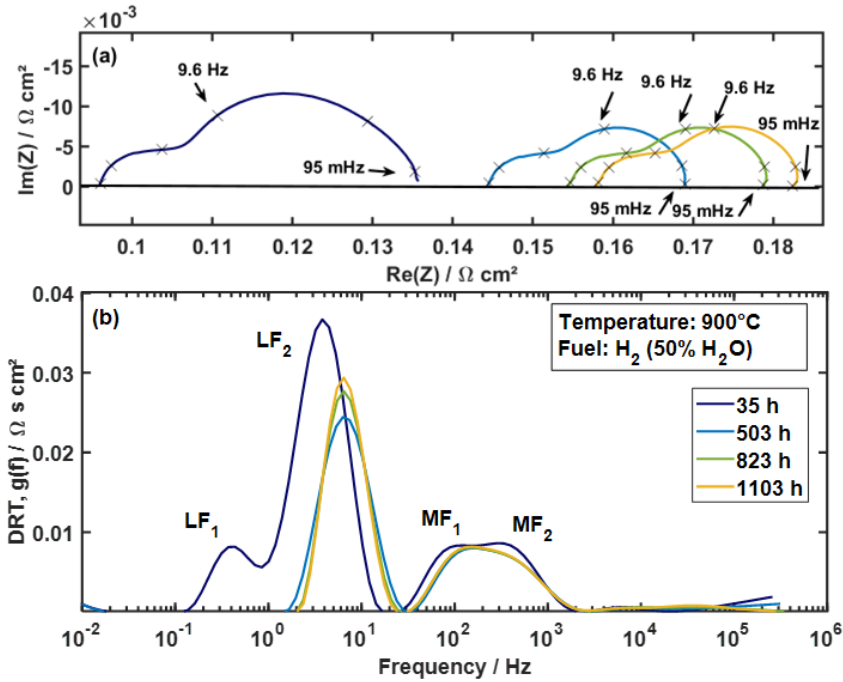


Figure 4.20: (a) Time evolution of impedance spectra of the Ni/GDC anode of Cell 3 (IS1-429_V1.2_1) under OCV at 900 °C in a 1:1 $\text{H}_2/\text{H}_2\text{O}$ mixture. (b) Corresponding DRTs. All values are divided by 2 to represent single-electrode contributions. Adapted and modified from (4).

in Section 4.2.1.2. Considering the applied temperature and humidity, surface diffusion is possible. Ni spreading and splitting phenomena have been reported on both Ni/GDC and Ni/YSZ electrodes (186, 298). Consequently, additional active reaction sites could form from Ni deposited on GDC surfaces within the porous interlayer.

The distributions of Ce and Ni were analyzed via EDS, as shown in Figure 4.22. From left to right, the SEM image, overall EDS mapping, and elemental distributions of Ce and Ni are presented for cell 1 (a1–a4) and cell 2 (b1–b4). SEM images acquired using an SE detector show no clear contrast between the Ni and GDC phases. In cell 1, the particles in both the GDC interlayer and the Ni/GDC anode layer are, on average, smaller than those in cell 2. The contrast observed in the YSZ substrate of cell 1 is attributed to local depth variations resulting from sample fracture during preparation.

EDS mappings indicate interdiffusion of Gd and Ce into the YSZ substrate. No Ni was detected within the porous GDC interlayer. However, since EDS is typically insensitive to very low

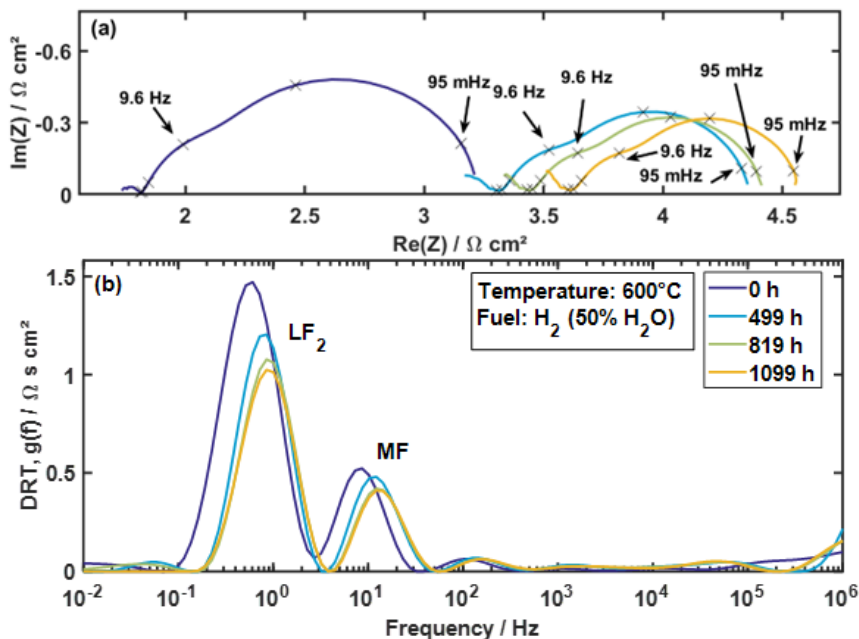


Figure 4.21: (a) Time evolution of reference impedance spectra of Ni/GDC anode of Cell 3 (IS1-429_V1.2_1) under OCV at 600 °C in a 1:1 $\text{H}_2/\text{H}_2\text{O}$ mixture. (b) Corresponding DRTs. All values are divided by 2 to represent single-electrode contributions. Adapted and modified from (4).

mass fractions (below approximately 1%) and a large fraction of the cross-section is intergranular porosity, Ni deposition on the GDC surfaces cannot be excluded. Given the high activity of nanoscale electrocatalysts, performance improvement due to Ni transport into the interlayer remains plausible despite the absence of direct EDS evidence.

The reconstructed electrodes of cells 1 and 2 are shown in Figure 4.23. Due to the strong similarity to cell 2, cell 3 is not presented here. Data acquisition and segmentation were carried out by Dr. Florian Wankmüller at LEM, KIT. The segmentation quality is excellent, as illustrated in Figure 4.23(a, d). The Ni/GDC layer of cell 1 exhibits a finer microstructure, as smaller Ni particles are observed in Figure 4.23(b). By visual inspection, no distinct morphological changes are present in the GDC phases.

The post-segmentation analysis was performed at IAM-ET using an in-house MATLAB® code described in (69). The microstructural parameters are summarized in Table 4.4. The reported tortuosities represent effective transport parameters for electronic, ionic, and gas phase conduction (69). All three cells exhibit similar compositions, with deviations of less than 1% in the volume fractions of all three phases.

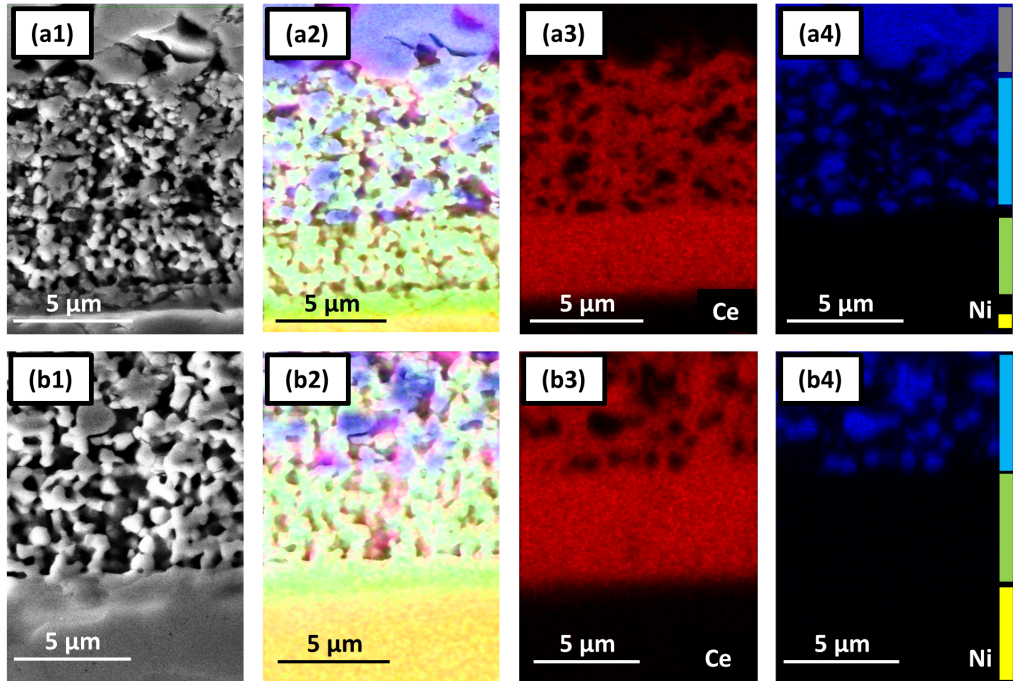


Figure 4.22: SEM/SE images and EDS mappings of (a1–a4) Cell 1 (IS1-427_V1.2_1) and (b1–b4) Cell 2 (IS1-424_V1.2_1). From left to right: (1) SE images (1.3 kV), (2) overlapped EDS mappings of Ni (blue), Ce (red), Gd (green), Y (orange), and Zr (yellow), (3) Ce mapping, and (4) Ni mapping. In (a4) and (b4), the YSZ layers are highlighted in yellow, the GDC layers in green, the Ni/GDC layers in blue, and the Ni contact layer in gray. Adapted from (4).

With increasing operating time, the TPB density decreased by 10%, from 2.16 to $1.94 \mu\text{m}^{-2}$ after 250 h, and further to $1.65 \mu\text{m}^{-2}$ after 1100 h at 900°C , corresponding to a total reduction of 24%. The DPB density (GDC–pore) decreased by 9.3% in cell 2, and further from 1.77 to $1.43 \mu\text{m}^{-1}$ in cell 3, resulting in an overall decrease of 27%.

During the first 250 h, TPB loss is more pronounced, whereas DPB reduction dominates during the subsequent 860 h. These changes in both TPB and DPB densities clearly indicate electrode degradation. The increasing tortuosity of the GDC phase, τ_{GDC} , also indicates reduced ionic and electronic conductivity. The only microstructural parameter that could suggest a possible improvement in R_{Pol} is the pore diameter, d_{pore} . However, the contribution of gas diffusion was already excluded. Based on these results, cell aging would be expected instead of the improvements observed in the electrochemical measurements.

Changes may occur on the nanometer scale (298, 186), below the resolution of FIB-SEM. Sciazko (187) reported multiscale microstructural evolution of Ni/GDC in SOFC operation.

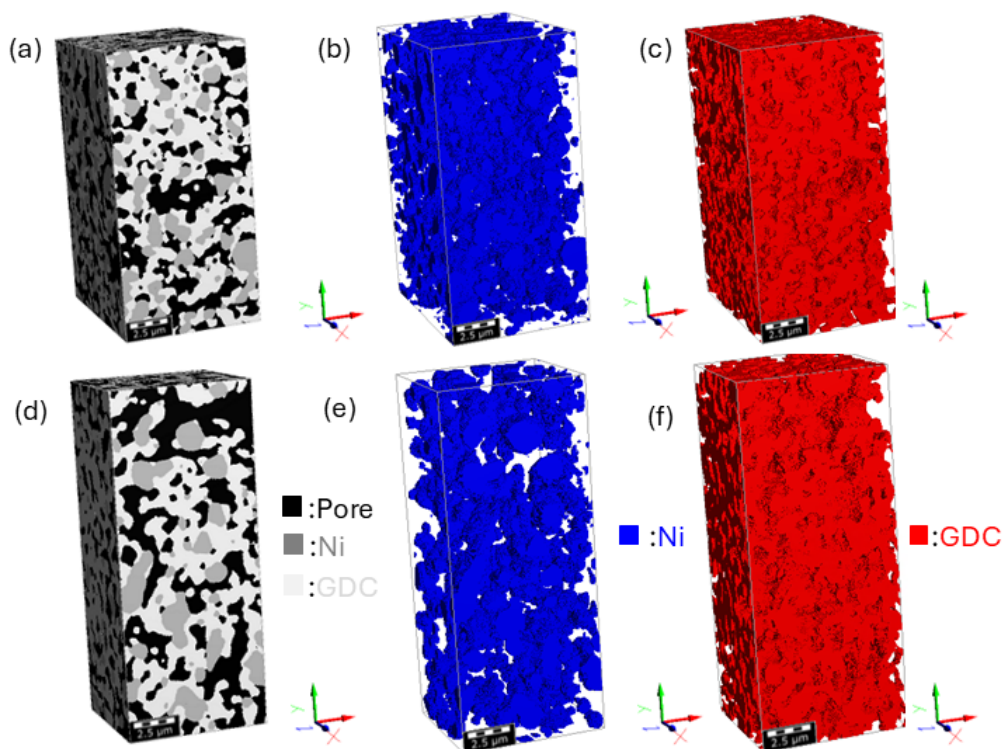


Figure 4.23: Reconstructed electrodes of (a) cell 1 (IS1-427_V1.2_1) and (d) cell 2 (IS1-424_V1.2_1) shown in grayscale. The separated phases are displayed individually: Ni in blue and GDC in red, presented in (b, c) for Cell 1 and in (e, f) for Cell 2.

They investigated an electrolyte-supported cell consisting of an LSCF cathode, an electrolyte, a Ni/GDC anode, and a Ni contact layer. The polarization resistance increased by 50% after 100 h of operation at a current density of 0.2 A cm^{-2} with a gas supply of 40% H_2 , 20% H_2O and 40% N_2 at 800 °C. Contrary to the worsening electrochemical performance, structural analysis revealed higher TPB and DPB densities. This apparent conflict was attributed to electrode inhomogeneity after testing. Significant GDC migration and the formation of nano-sized GDC layers were observed on Ni surfaces. The newly formed Ni/GDC interfaces appeared closer to the contact layer, whereas near the electrolyte, a reduction in GDC content and in both DPB and TPB densities was observed.

To investigate potential nanoscale structural changes, STEM analysis was conducted on cell 3, which had been aged for 1,100 h at 900 °C. The analysis focused on three regions: the GDC interlayer (Window I), the Ni/GDC anode layer (Window III), and the transition zone between the two layers (Window II). Each of these areas was thinned to approximately 100 nm using

Table 4.4: Microstructural parameters of cells 1–3 derived via FIB-SEM.

Parameter	Cell 1, IS1-427_1	Cell 2, IS1-424_1	Cell 3, IS1-429_1
Testing durations	Reduced	250 h	1100 h
Reconstructed volume / μm^3	1686	1542	5104
$\varepsilon_{\text{pore}} / \%$	36	38	37
$\varepsilon_{\text{GDC}} / \%$	44	42	41
$\varepsilon_{\text{Ni}} / \%$	20	20	22
$l_{\text{TPB}} / \mu\text{m}^{-2}$	2.16	1.94	1.65
$A_{\text{Ni-Pore}} / \mu\text{m}^{-1}$	0.59	0.33	0.34
$A_{\text{GDC-Pore}} / \mu\text{m}^{-1}$	1.95	1.77	1.43
$\tau_{\text{pore}} / -$	2.47	2.43	2.57
$\tau_{\text{GDC}} / -$	2.32	2.45	3.81
$d_{\text{pore}} / \mu\text{m}$	0.43	0.55	0.67
$d_{\text{GDC}} / \mu\text{m}$	0.50	0.56	0.67
$d_{\text{Ni}} / \mu\text{m}$	0.38	0.65	0.85
$r_{\text{ct}} / \cdot 10^{-4} \Omega\text{cm}^3$	8.99	4.73	4.72

a Helios G4FX via FIB milling. STEM imaging was performed by Dr. Tibor Lehnert using a high-angle annular dark-field detector (HAADF-STEM) to provide detailed structural and compositional information.

The results for Window I and II are presented in Figure 4.24. Data for Window III are not shown due to the similarity to Window II. The HAADF images reveal nano-pores between individual GDC grains (highlighted by red ovals). EDS elemental mapping of Ni, Ce, and Gd was performed using an OSIRIS ChemiSTEM microscope. The Ce and Gd maps of Window I (Figure 4.24(a)) confirm that the material in this region consists only of GDC. Ni was not detected in Window I. However, its presence on GDC surfaces cannot be completely excluded, as it may be below the detection limit or removed during FIB thinning.

In the overlapping region between the GDC interlayer and the Ni/GDC anode layer (Window II, Figure 4.24(b)), similar nanopores were observed. The presence of nano-pores between GDC particles appears limited, and their influence on electrode performance is difficult to quantify. Given their small number, they are unlikely to contribute significantly to increasing the GDC surface area.

Overall, the minor microstructural changes observed in these STEM studies are unlikely to account for the measured improvement in Ni/GDC electrode performance. The most likely explanation is the activation of GDC surfaces within the porous interlayer by inter-diffused Ni, thereby enhancing

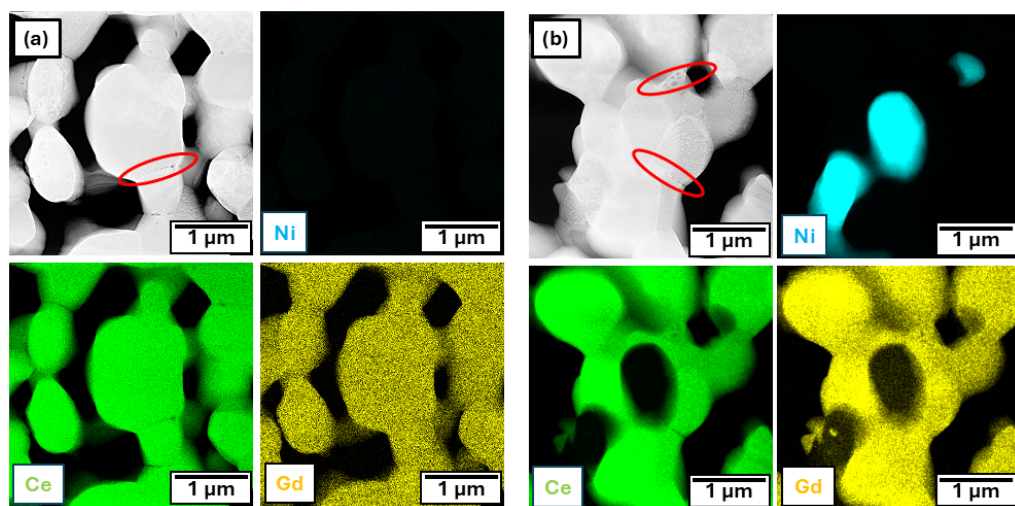


Figure 4.24: STEM-EDS results (200 kV high-angle annular dark-field [HAADF]) for (a) Window I and (b) Window II. The images in (a) and (b) are shown clockwise: STEM image (no contrast between GDC and Ni due to similar average atomic masses of CeO_2 and Ni), Ni distribution in blue, Gd distribution in yellow, and Ce distribution in green. Adapted from (4).

electrochemical activity and leading to the observed increase in performance. As reported by Kullmann et al. (78), the polarization resistance decreased from 0.196 to $0.07 \Omega\text{cm}^2$ (-64.3%) at 700°C after infiltration of a pure GDC layer with a $4.6 \text{ wt}\%$ $\text{Ni}(\text{NO}_3)_2$ solution. No significant changes were observed in the corresponding SEM images, while the EDS signals associated with Ni were very weak and could not be quantified reliably. In the present study, the samples exhibited a smaller improvement in polarization resistance (approximately -40% in Figure 4.21). It is therefore assumed that an even smaller amount of Ni was present in the GDC interlayer, resulting in Ni concentrations below the detection limit of EDS.

4.4.1.1.2 Cell from V1.5a Operated at 50% Humidity in Fuel The cell IS1-470_V1.5a presented in this section consists of an electrolyte, two Ni/GDC layers from usual Jülich paste sintered at 1200°C , and two Ni contact layers with a particle size of $0.5 \mu\text{m}$.

Given that structural analysis cannot identify the impact of a GDC interlayer in screen-printed cells, a counterpart experiment was conducted using the cell IS1-470_V1.5a. The cell was first reduced at 650°C and then heated to 900°C . Due to deteriorating data quality, continuous impedance measurements were stopped after 130 h, and the cell was cooled under a reducing atmosphere. The impedance evolution and corresponding DRTs at 900°C and 600°C are presented in Figure 4.25.

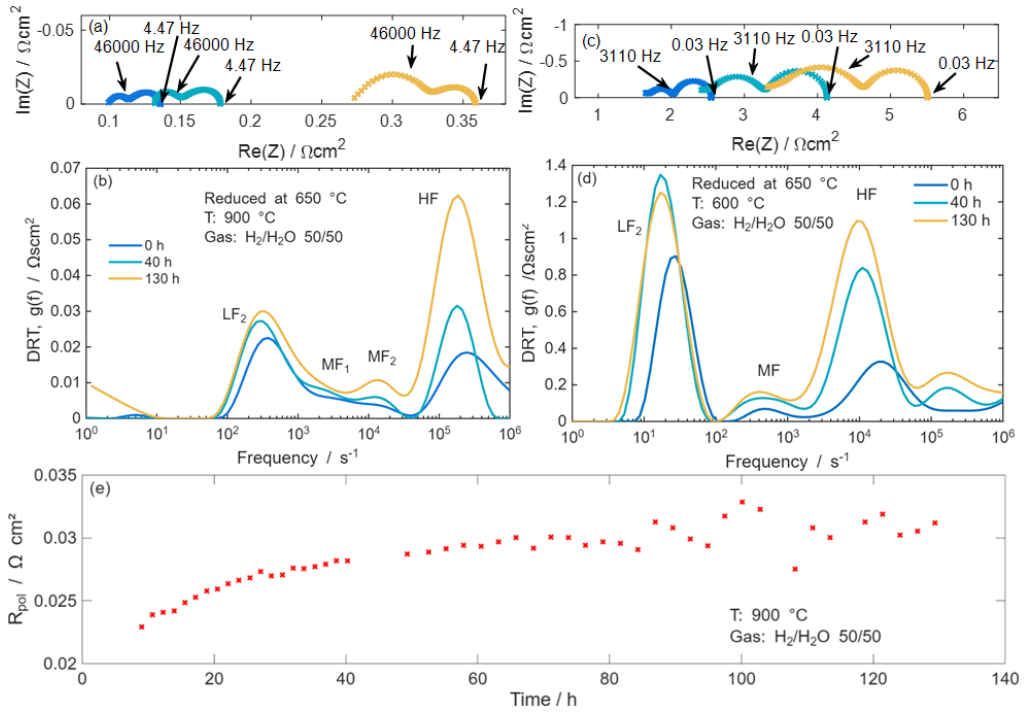


Figure 4.25: Time evolution of (a) impedance spectra and (b) corresponding DRTs of the electrode of cell IS1-470_V1.5a operated at 900 °C under a 50:50 steam/ H_2 gas mixture. Time evolution of (c) reference impedance spectra and (d) corresponding DRTs. (e) The evolution of polarization resistance at 900 °C against time. Adapted from (7).

At 900 °C, the DRT in Figure 4.25(b) indicates degradation across all visible processes. For the LF_2 process, aging during the first 40 h is more pronounced than in the subsequent 90 h. In contrast, the MF_2 process exhibits steady degradation throughout the entire measurement period. The most significant degradation occurs in the HF process and is unrelated to the electrode.

Considering the difference between the impedance at 10,000 Hz and the maximum to be the polarization resistance, Figure 4.25(e) shows a sharp increase during the first 40 h (from 0.023 Ωcm^2 to 0.028 Ωcm^2) in R_{pol} , followed by a slower increase and eventual plateau after 80 h. These findings suggest that the electrode reaches a stable electrochemical state at 900 °C, indicating that potential microstructural changes during this period do not significantly affect the electrochemical response of the electrode.

A similar degradation pattern was observed in the three reference measurements at 600 °C (Figure 4.25(c, d)). Clear degradation occurred in all three visible processes. CNLS fitting using three RQ elements revealed a sharp increase in the LF_2 process during the first 40 h, from

0.45 Ωcm^2 to 0.75 Ωcm^2 , followed by a smaller increase of only 0.05 Ωcm^2 over the next 90 h. The MF process followed a similar trend, while the HF process exhibited uniform, continuous degradation.

Despite the limited test duration, no improvement in polarization resistance was observed. These results support the hypothesis that Ni surface diffusion into the porous GDC layer may be responsible for the improved performance sometimes observed in similar electrode systems with an extra interlayer. However, since this study focuses on Ni/GDC electrode degradation, processes unrelated to the electrode but affecting impedance should be excluded. Therefore, cells used for AST and modeling should not contain an interlayer.

4.4.1.2 Durability at 800 °C

As the test results of IS1-424, IS1-470, and IS1-429 indicate, the porous GDC layer may also act as an electrochemically active electrode. Because of its proximity to the electrolyte, the activity of this layer dominates the overall electrode performance. To verify this hypothesis, our project partner FZJ fabricated a reference variant (Ref1) consisting of a screen-printed GDC (sintered at 1300 °C) layer, with a screen-printed NiO contact layer applied on top.

At 800 °C, two cells, IS1-443_Ref1 and IS1-443_V1.2, were operated in hydrogen with 50% humidity for 980 h. To investigate the potential contribution of Ni surface diffusion via suppressing aging effects associated with the formation and transport of volatile Ni species, one cell, IS1-445_V1.2, was reduced at 650 °C and subsequently heated to 800 °C, where it was operated in hydrogen with 10% humidity for 390 h.

4.4.1.2.1 Cell from Ref1 at 50% Humidity in Fuel The cell IS1-443_Ref1, presented in this section, consists of an electrolyte with two pure GDC layers sintered at 1300 °C and two contact layers with a particle size of 0.5 μm .

The impedance spectra, corresponding DRTs, and polarization resistance of the electrode against time for cell IS1-443_Ref1 are presented in Figure 4.26(a-c). The ohmic resistance increased from 0.16 Ωcm^2 to 0.21 Ωcm^2 (+31%) within the first 390 h. During the following 590 h, it rose further to 0.44 Ωcm^2 (+175%), corresponding to a degradation rate approximately eight times higher than in the initial period. A similar accelerated increase was observed in the polarization resistance.

In the first 26 h (system time offset: 50 h), the LF process degraded slowly, after which it improved slightly, possibly due to Ni particle redistribution within the GDC layer, similar to that observed in 4.4.1.1.1. Until 390 h, the low-frequency process LF had already decreased relative to its initial

state, and the two middle-frequency processes showed only minor changes. In the subsequent 590 h, however, obvious degradation occurred across all processes, with LF and MF₂ being most dominant as indicated in Figure 4.26(b).

The temporal evolution of the polarization resistance at 800 °C is shown in Figure 4.26(c). During the first 20 h, a slight increase was observed, followed by a slight decrease until about 150 h. Between 150 and 300 h, the resistance remained at a plateau of approximately 0.04 Ωcm^2 . After 300 h, it rose sharply until 550 h, reaching a second plateau of about 0.14 Ωcm^2 .

During this latter plateau, each time the cell was cooled to 600 °C and subsequently reheated to 800 °C, the R_{pol} temporarily dropped to $\sim 0.125 \Omega\text{cm}^2$, and returned to the plateau within 20 h. This reversible recovery was observed consistently after all three references.

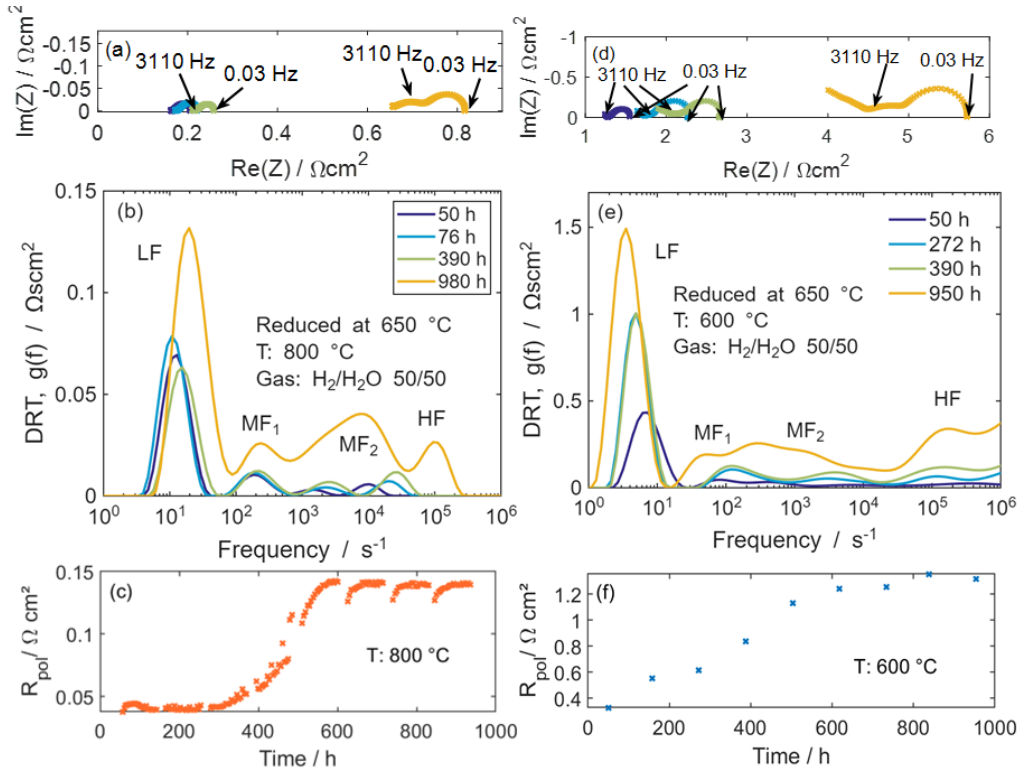


Figure 4.26: Time evolution of (a) impedance spectra, (b) corresponding DRTs, and (c) polarization resistance of the electrode of cell IS1-443_Ref1 operated at 800 °C under a 50:50 steam/H₂ gas mixture. Time evolution of (d) reference impedance spectra, (e) corresponding DRTs, and (f) polarization resistance at 600 °C.

Figure 4.26(d-f), presenting the reference measurements, reveals an overall similar but slightly different trend. In particular, no improvement in polarization resistance, especially in the LF process, was observed when comparing the spectra taken at 50 h and 390 h. The cause of this discrepancy remains unclear. One possibility could be differences in electrode penetration depth across temperatures.

A potential explanation for the sudden degradation may be the strong chemical expansion of the GDC layer under high-temperature reducing conditions (299, 300, 301). Unlike the usual Jülich paste used in other V1 cells (containing ~ 40 vol.% GDC in the electrode), cells from Ref1 featured a pure GDC electrode with ~ 70 vol.% GDC. In the absence of Ni particles that dilute the net chemical expansion, they likely experienced stronger expansion. After approximately 300 h of operation, the accumulated lattice strain may have led to dislocation formation and micro-crack initiation, thereby weakening the adhesion between the GDC electrode and the electrolyte and degrading overall cell performance.

The observed recovery can be attributed to the reversible nature of GDC chemical expansion (301, 302). At $600\text{ }^{\circ}\text{C}$, the expansion is significantly weaker, allowing partial relaxation of mechanical fatigue. This reappears upon reheating to $800\text{ }^{\circ}\text{C}$, leading to an increase in the R_{pol} . Compared to the pristine electrode of cell IS1-442_Ref1 shown in Figure 4.27(a, c), no significant changes were observed in the cross-sectional images in Figure 4.27(b, d) for cell IS1-443_Ref1. No large-scale delamination, extended micro-cracking, or other major structural failure was found.

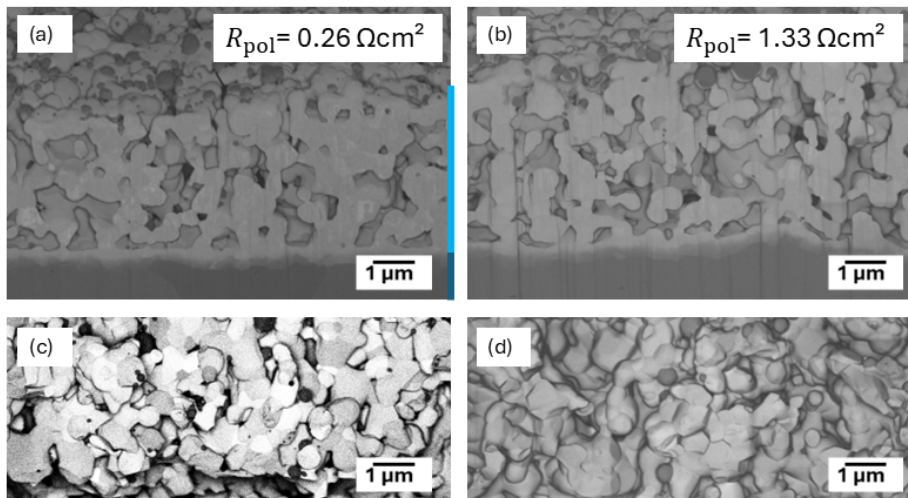


Figure 4.27: SEM/BSE images of (a) polished and (c) fractured cross-section of pristine cell IS1-442_Ref1. SEM/BSE images of (b) polished and (d) fractured cross-section of cell IS1-443_Ref1 operated at $800\text{ }^{\circ}\text{C}$ for 980 h. The polarization resistances are obtained under nominal conditions.

In summary, an electrode consisting solely of porous GDC with a Ni contact layer exhibited a low polarization resistance of $0.26 \Omega\text{cm}^2$. This phenomenon is likely associated with the presence of nanoscale Ni particles that activate the GDC surface, potentially via surface diffusion. This mechanism may also account for the long-term improvement observed in tests IS1-424, IS1-429, and IS1-443. During operation, the cell initially showed a slight increase in polarization resistance within the first 26 h, followed by a prolonged improvement up to 390 h. At longer operating times, chemical expansion appeared to become the dominant degradation mechanism, leading to a pronounced increase in polarization resistance that outweighed the potential performance improvement.

4.4.1.2.2 Cell from V1.2 at 50% Humidity in Fuel The cell IS1-443_V1.2, presented in this section, consists of an electrolyte, two GDC interlayers sintered at 1300°C , two Ni/GDC layers from usual Jülich paste sintered at 1400°C , and two Ni contact layers with a particle size of $0.5 \mu\text{m}$.

Cell IS1-443_V1.2, operated under 800°C in hydrogen with 50% humidity, exhibited a different aging behavior from 900°C . As shown in Figure 4.28(a, b), four main processes, including an HF process, were visible in the DRT spectra. Until 935 h, the MF process degraded the most, followed by the LF_2 process. In contrast, the LF_1 process remained almost unchanged, suggesting a relatively constant gas diffusion loss throughout the test.

Due to strong overlap, it is not possible to determine which MF process is primarily responsible for the degradation. The small peak between 1000 and 10,000 Hz may correspond to the decaying side peak observed in the transmission line model simulation presented in Figure 2.8(c). Thus, changes in this feature are neglected.

The polarization resistance, determined from the distance between the two intersections of the impedance arc with the real axis, is shown in Figure 4.28(c). In the first 50 h, the polarization resistance increased sharply from $0.065 \Omega\text{cm}^2$ to $0.09 \Omega\text{cm}^2$. After a slight decrease, it began to rise again at 150 h, increasing by $0.01 \Omega\text{cm}^2$ over the subsequent 800 h. Despite a temporary improvement still being observed, it was much weaker than at 900°C , possibly due to reduced surface diffusion at the lower temperature.

The reference measurements, presented in Figure 4.28(d, e), confirm this aging behavior. At 600°C , the two LF processes merged into a single peak, which showed only degradation. The MF contribution degraded strongly, with its peak shifting to lower frequencies and partially overlapping with the LF process. The polarization resistance in Figure 4.28(f) shows a sharp increase before 150 h, followed by a slower rise, consistent with the trend observed at 800°C .

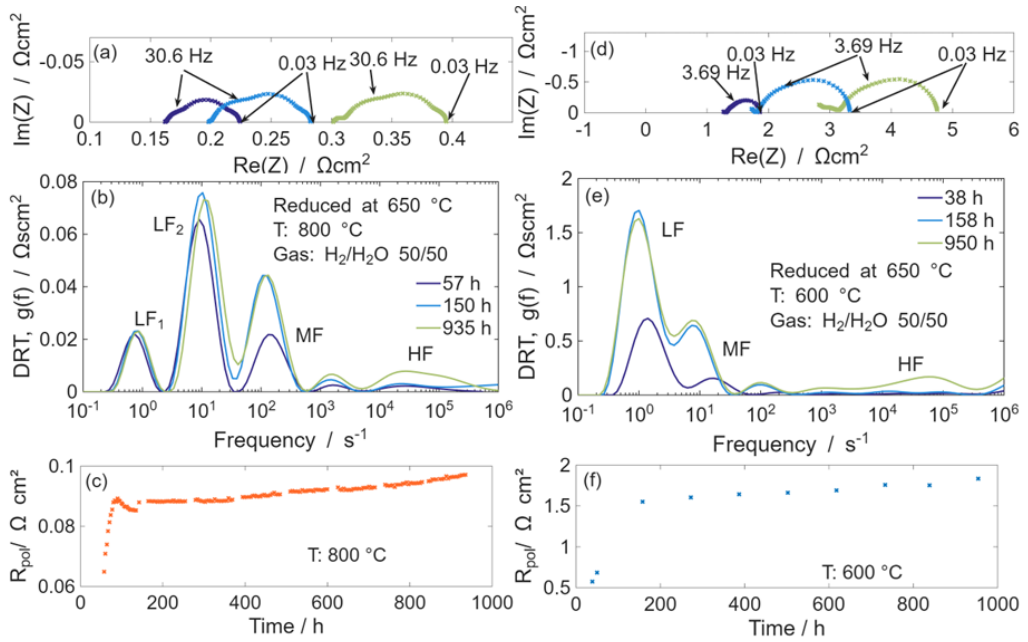


Figure 4.28: Time evolution of (a) impedance spectra, (b) corresponding DRTs, and (c) polarization resistance of the electrode of cell IS1-443_V1.2 operated at 800 °C under a 50:50 steam/H₂ gas mixture. Time evolution of (d) reference impedance spectra, (e) corresponding DRTs, and (f) polarization resistance at 600 °C. Adapted from (7).

However, due to the lack of a measurement around 150 h, it remains unclear whether the temporary improvement is also visible at 600 °C.

Post-test analysis, presented in Figure 4.29, revealed significant microstructural changes compared to the pristine cell IS1-442_V1.2, shown in Figure 4.11(b, d). After 935 h at 800 °C, the Ni particles markedly coarsened. In particular, the nano-sized Ni particles previously observed on the surface of the GDC phase disappeared, indicating a less catalytically active surface. Furthermore, the GDC matrix had sintered together and coated the Ni particles, suggesting a reduction in both TPB and DPB densities.

FIB-SEM confirmed these observations. Dr. Matthias Wieler performed the reconstruction and segmentation at Bosch, Renningen. The further analysis was carried out with the in-house MATLAB[®] code at our institute. The derived structural parameters are summarized in Table 4.5. The average Ni particle size increased from 0.51 μm to 0.59 μm , while the GDC particle size remained nearly constant. The TPB density decreased from 4.27 μm^{-2} to 3.74 μm^{-2} (-13%), and the DPB density decreased by 16%, from 1.92 μm^{-1} to 1.61 μm^{-1} . The increased tortuosity of the GDC phase, equaling a degraded electrode conductivity, partly contributed to the enlargement of

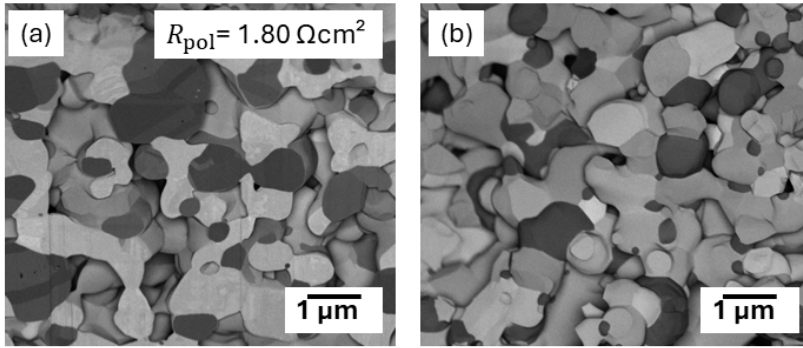


Figure 4.29: SEM/BSE images of (a) polished and (b) fractured cross-section of cell IS1-443_V1.2. Dark gray indicates Ni, and bright gray indicates GDC. The polarization resistance is obtained under nominal conditions. Adapted from (7).

the MF peak. These microstructural changes are consistent with the degradation trends identified in the impedance analysis.

Table 4.5: Structural parameters of cells from V1.2 before and after operation.

Parameter/Cell ID	IS1-442_V1.2	IS1-443_V1.2
Condition	Reduction 650 °C	Aging at 800 °C 950 h
Reconstructed volume / μm^3	2672	1321
$\varepsilon_{\text{pore}} / \%$	36	37
$\varepsilon_{\text{GDC}} / \%$	42	41
$\varepsilon_{\text{Ni}} / \%$	22	22
$l_{\text{TPB}} / \mu\text{m}^{-2}$	4.27	3.74
$A_{\text{Ni-Pore}} / \mu\text{m}^{-1}$	1.26	0.65
$A_{\text{GDC-Pore}} / \mu\text{m}^{-1}$	1.97	1.62
$\tau_{\text{Pore}} / -$	2.25	2.32
$\tau_{\text{GDC}} / -$	2.87	3.52
$\tau_{\text{Ni}} / -$	Isolated	Isolated
$d_{\text{pore}} / \mu\text{m}$	0.26	0.39
$d_{\text{GDC}} / \mu\text{m}$	0.54	0.53
$d_{\text{Ni}} / \mu\text{m}$	0.51	0.59
$r_{\text{ct}} / \cdot 10^{-4} \Omega\text{cm}^3$	7.50	2.81

Due to the absence of a quantitative physical model linking TPB and DPB densities, as well as Ni activation, to overall electrochemical performance, it cannot be conclusively determined which factor dominates aging.

4.4.1.2.3 Cell from V1.2 at 10% Humidity in Fuel The cell IS1-443_V1.2, presented in this section, consists of an electrolyte, two GDC interlayers sintered at 1300 °C, two Ni/GDC layers from usual Jülich paste sintered at 1400 °C, and two Ni contact layers with a particle size of 0.5 μm .

The cell IS1-445_V1.2 was operated for 980 h at 800 °C under reduced humidity (10%) to emphasize the impact of Ni surface diffusion. It exhibited a markedly different aging behavior compared to its counterpart tested at 50% humidity. After an initial degradation between 60–70 h, a long-term improvement in polarization resistance was observed. As shown in Figure 4.30(a), the arc in the low-frequency region shrank significantly over time, consistent with reduced contributions of the LF_2 peak in Figure 4.30(b). The MF process degraded strongly between 50–170 h but subsequently stabilized. Notably, LF_2 continued to improve throughout the test, and by the end of 980 h, the polarization resistance had nearly returned to its initial value, as presented in Figure 4.30(c).

Reference measurements at 600 °C revealed a different trend. As shown in Figure 4.30(d, e), both LF and MF processes degraded significantly in the first 140 h, while the measurements at 176 h and 405 h indicated stable polarization resistance. Figure 4.30(f) displays a clear increase at 600 °C, in contrast to the improvement observed at 800 °C under 10% H_2O . This inconsistency can be attributed to the different temperature dependencies of the LF_2 and MF processes. The resistance of the LF_2 process, fitted with an RQ element from the reference measurements, showed a similar trend to R_{pol} at 800 °C, as illustrated in Figure 4.31. This confirms the consistency of the test results and highlights the dominant degradation from the MF process.

One possible explanation for the improvement is that the formation of volatile Ni species and their diffusion in the gas phase are suppressed by low humidity (27), thereby hindering particle migration and agglomeration. In this case, surface diffusion of Ni onto GDC may dominate. It can be concluded that an operating temperature of 800 °C remains too high. The continued improvement in polarization resistance suggests that Ni surface diffusion on GDC still strongly competes with other degradation mechanisms.

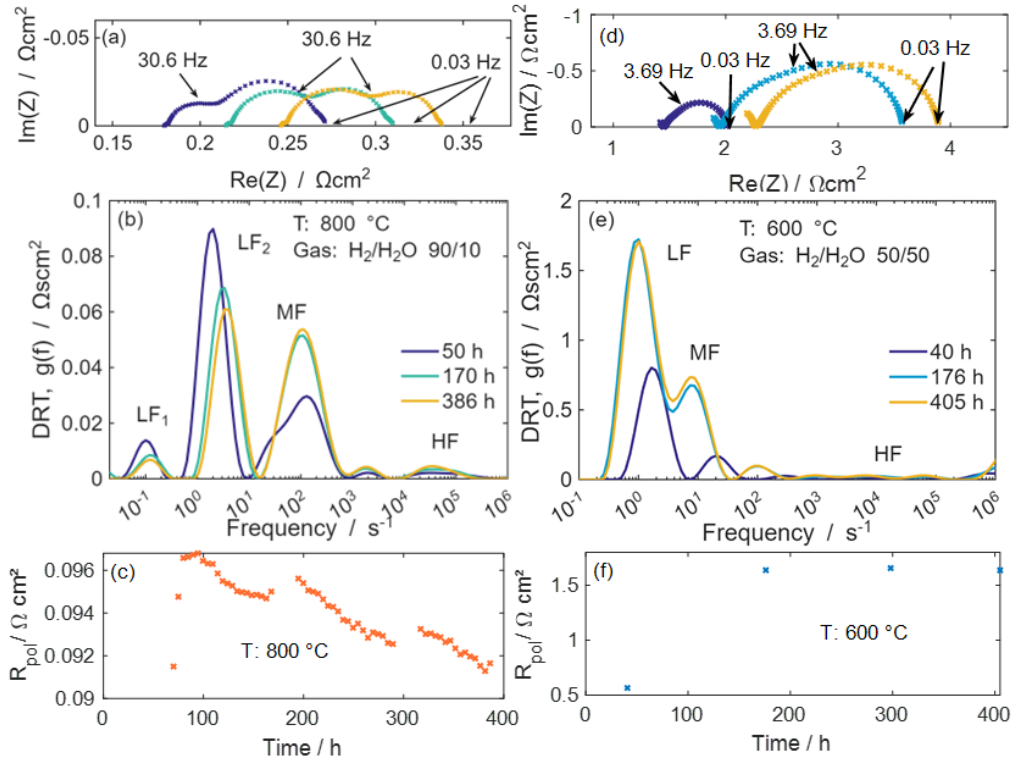


Figure 4.30: Time evolution of (a) impedance spectra, (b) corresponding DRTs, and (c) polarization resistance of the electrode of cell IS1-445_V1.2 operated at 800 °C under a 10:90 steam/H₂ gas mixture. Time evolution of (d) reference impedance spectra, (e) corresponding DRTs, and (f) polarization resistance at 600 °C. Adapted from (7).

4.4.1.3 Durability at 750 °C and Lower

In addition, several V1 cells were operated at intermediate temperatures between 600 °C and 750 °C. A summary of the tested cells, along with corresponding operating conditions and durations, is provided in Table 4.3.

The impedance measurements at 600–750 °C exhibited similar behavior to that of cell IS1-443_V1.2 (No. 5), as shown in Figure 4.28. The degradation occurs mainly in LF and MF processes. Across all four cells (No. 7-10), no improvement was observed. Therefore, a detailed presentation is omitted. Since MF includes the unassigned process MF₂, it should be excluded when describing electrode degradation, and using LF₂ as the indicator is reasonable. Due to the lack of structural parameters, a simplified ECM consisting of five RQ elements was applied instead of the one presented in Figure 4.18. The fitting was performed using reference measurements

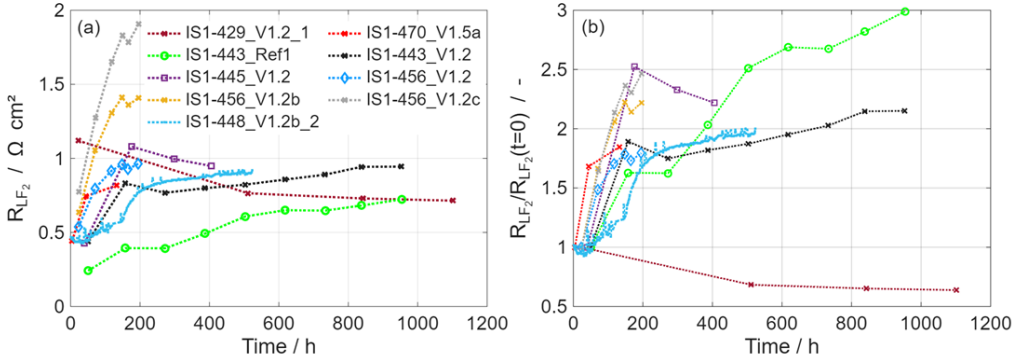


Figure 4.31: Time evolution of the fitted R_{LF_2} values of the V1 variant from the reference measurements, shown as (a) absolute and (b) relative values. Cells No. 2–3 (IS1-429_V1.2_1 and IS1-470_V1.5a) were operated at 900 °C in humidified hydrogen (50% H_2O). Cells No. 4–5 (IS1-443_Ref1 and IS1-443_V1.2) were operated at 800 °C in humidified hydrogen (50% H_2O), while Cell No. 6 (IS1-445_V1.2) differed only in humidity (10% H_2O). Cells No. 7–9 (IS1-456_V1.2, IS1-456_V1.2b and IS1-456_V1.2c) were operated at 750 °C in humidified hydrogen (50% H_2O). Cell No. 10 (IS1-448_V1.2b_2) was operated at 600 °C in humidified hydrogen (50% H_2O). Adapted from (7).

to directly compare cells operated under different conditions. The fitted values R_{LF_2} are plotted against time in Figure 4.31, both in absolute and relative terms. Owing to the absence of reference measurements, the results from IS1-424_V1.2_1 (No. 1) are not included. Given the excellent reproducibility, the IS1-429_V1.2_1 (No. 2) curve yields comparable results.

At 900 °C, the evolution of R_{LF_2} is consistent with R_{pol} , as described in Section 4.4.1.1. However, at 800 °C under 10% fuel humidity, their behavior diverged. This discrepancy was attributed to the dominance of degradation in the MF process and its potentially higher activation energy. A closer look at the two tests at 800 °C (IS1-443_V1.2 and IS1-445_V1.2 in Figure 4.31) shows that R_{LF_2} first increased and then decreased within the initial 300 h. Surprisingly, during this early phase, the cell operated under lower humidity exhibited stronger degradation, further indicating the complexity of the cell system containing a GDC interlayer.

At 750 °C, cell IS1-456_V1.2 exhibited the highest resistance to aging compared to IS1-456_V1.2b and IS1-456_V1.2c, with an increase of $0.03 \Omega \text{ cm}^2$ in R_{LF_2} , corresponding to $0.55 \Omega \text{ cm}^2$ when measured at 600 °C. This is likely related to the interlayer, which acts as part of the active electrode and affects the overall impedance. In contrast, cell IS1-456_V1.2b showed more pronounced degradation, with R_{LF_2} increasing from 0.65 to $1.42 \Omega \text{ cm}^2$ (+125%). Although Ni phase changes may have less impact on cell IS1-456_V1.2, they likely altered the TPB and DPB densities in the other 2 cells. The strongest degradation was observed in cell IS1-456_V1.2c (+150%), which had a coarser Ni contact layer. This could be attributed to a reduction in the active electrode area due to Ni coarsening in the current collector layer.

The durability test results from IS1-454 are not fully reliable because the cells within the same assembly exhibited significant differences, as discussed in Section 4.1. Therefore, these results are excluded from Table 4.3 and Figure 4.31. A brief qualitative description is provided here instead. Cell IS1-454_V1.2b was operated at 700 °C for 880 h, and degradation was primarily limited to low-frequency processes. This cell was selected for further structural analysis, and SEM images of the electrode are shown in Figure 4.32(e, f). The value of the LF_2 process shown in Figure 4.32(e) was derived from a measurement conducted after the cell was demounted from the assembly and reassembled between two similar cells.

Additionally, cells IS1-448_V1.2b_1/2 were operated at 600 °C for up to 550 h, showing continuous LF-related increases in polarization resistance without improvement. The cell IS1-448_V1.2b_1 was removed after 130 h, and IS1-448_V1.2b_2 after 550 h. The total increase for the later was $0.41 \Omega\text{cm}^2$ (+95%), indicating significantly slower aging compared to 750 °C. The SEM images of these two cells are shown in Figure 4.32(a-d).

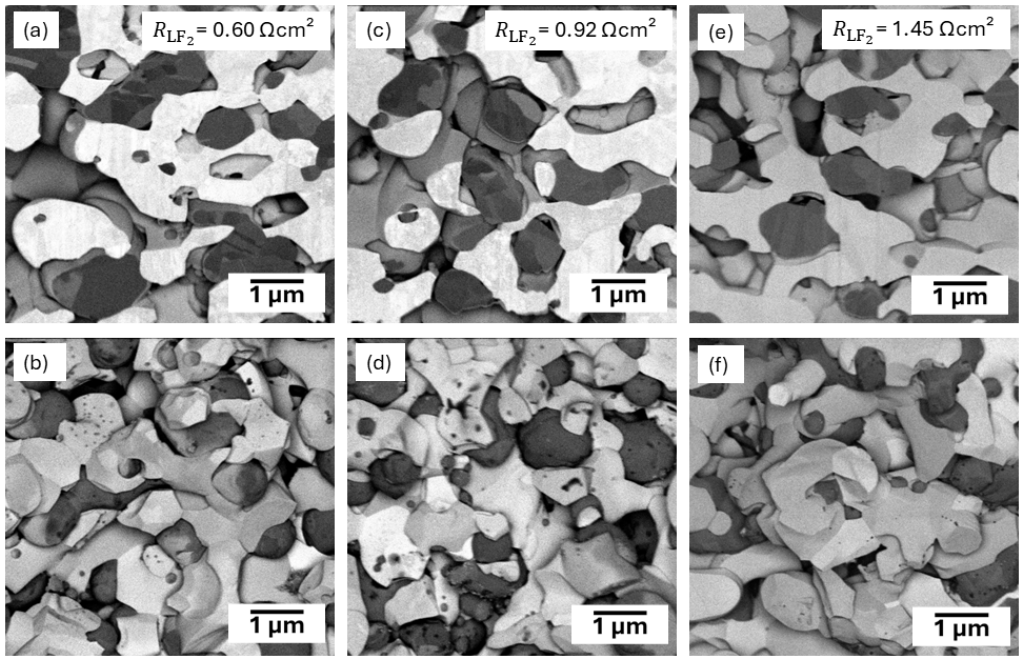


Figure 4.32: SEM/BSE images of polished and fractured cross sections of cell (a, b) IS1-448_V1.2b_1, which is operated at 600 °C for 130 h, and (c, d) IS1-448_V1.2b_2, operated for 500 h; and (e, f) cell IS1-454_V1.2b, aged at 700 °C for 880 h. The values of the LF_2 process are fitted from impedances under nominal conditions. Adapted from (7).

Compared to the pristine electrode of cell IS1-446_V1.2b shown in Figure 4.9(a), all three aged samples exhibit coarsening of Ni particles, likely equaling a reduction in TPB density. Another significant observation is the disappearance of nano-Ni particles from the GDC surface, resulting in less active DPB. No major differences were seen among the three operated cells. A 3D reconstruction is thus necessary to quantify the changes. This was carried out at LEM (KIT), and the initial image processing and segmentation were performed by Dr. Ardavan Makvandi using a newly developed automated Python-based script (12). Further data analysis was conducted at IAM-ET using in-house MATLAB[®] code. All comparisons in this work are made within datasets processed using the same script.

Table 4.6: Microstructural parameters of cells from V1.2b at different aging temperatures with 50% humidity in hydrogen.

Cell ID	IS1-446_V1.2b	IS1-448_V1.2b_1	IS1-448_V1.2b_2	IS1-454_V1.2b
Condition	Reduction 650 °C	600 °C for 130 h	600 °C for 500 h	700 °C for 880 h
$\varepsilon_{\text{pore}} / \%$	22	22	24	23
$\varepsilon_{\text{GDC}} / \%$	50	50	48	49
$\varepsilon_{\text{Ni}} / \%$	30	28	28	28
$l_{\text{TPB}} / \mu\text{m}^{-2}$	10.09	8.86	8.79	6.60
$A_{\text{GDC-Pore}} / \mu\text{m}^{-1}$	1.68	1.54	1.31	0.98
$d_{\text{pore}} / \mu\text{m}$	0.36	0.35	0.34	0.34
$d_{\text{GDC}} / \mu\text{m}$	0.56	0.57	0.57	0.58
$d_{\text{Ni}} / \mu\text{m}$	0.22	0.25	0.27	0.37
$r_{\text{ct}} / \cdot 10^{-4} \Omega\text{cm}^3$	3.32	4.32	6.70	11.5

The pristine cell exhibited the highest TPB density, which decreased by 22% to $8.86 \mu\text{m}^{-2}$ after 130 h of operation at 600 °C with 50% H₂O. Over the following 370 h, a slight further decrease of $0.07 \mu\text{m}^{-2}$ was observed. A similar trend was observed in DPB density, which declined by 8% during the first 130 h and by an additional 14% over the remaining period. Another parameter indicating aging is the Ni particle size, which increases from 0.22 to 0.25 μm (+13.6%) in the first 130 h, and further increases by 0.02 μm (+9.1%) up to 500 h. These results indicate faster degradation in the early phase, followed by a slower rate, consistent with the observed evolution of impedance.

In comparison, structural degradation was more severe in the cell aged at 700 °C. The TPB density dropped to $6.60 \mu\text{m}^{-2}$, corresponding to only 65% of its original value, while the DPB density decreased to 58% of the pristine level. An increase of 68.2% in Ni particle size, from 0.22 to 0.37 μm , is observed. These findings correlate well with the significant increase in $R_{\text{LF}2}$.

The GDC and pore phase seem to remain quite stable at both temperatures. The size values deviate by up to 0.01 μm , likely due to systematic error in data acquisition and processing.

In summary, the main degradation mechanisms for V1-variants at $\leq 700^\circ\text{C}$ include: (1) a reduction in TPB density, (2) a decrease in DPB density, and (3) a weakening of GDC surface activity due to the loss of nano Ni particles.

4.4.2 GDC-infiltrated Ni Skeleton Cells V6

Compared to screen-printed cells, infiltrated cells exhibit a finer electrode microstructure with significantly enhanced performance. The nanoscale microstructure of the infiltrated GDC, annealed only at 500°C , raises questions regarding its stability under nominal operating conditions. In particular, variant V6 presents an interesting case for studying the aging behavior and structural changes of the ultrafine GDC phase. To date, no other group has achieved comparable performance in a GDC-infiltrated Ni-skeleton cell (127, 128). Consequently, no study has established a link between impedance evolution and changes in the ultrafine GDC phase. In this section, cells were operated at $700\text{--}900^\circ\text{C}$ to investigate their sintering effects.

4.4.2.1 Durability at 900°C and 700°C with 50% Humidity in Fuel

All the cells discussed in this section are subvariants V6.1 and V6.5 of cell variant V6, which incorporates thick GDC interlayers and electrodes prepared by infiltrating GDC into a NiO skeleton sintered at $1,100^\circ\text{C}$. The two subvariants differ in the number of infiltration steps, with V6.1 and V6.5 undergoing nine and five infiltration steps, respectively. Initial electrochemical characterization and structural analyses confirmed the similarity between the two subvariants. Although these cells differ in the number of infiltration cycles, their electrode microstructures and aging characteristics are sufficiently similar to allow quantitative comparison within the scope of this work. The results presented in this section have been reported in (6).

For a systematic and comparative study, three cells from V6, named C.1, C.2, and C.3, were reduced under identical conditions at 650°C and subsequently heated to different operational temperatures:

- C.1: IS1-438_V6.5, demounted immediately after initial reduction and characterization.
- C.2: IS1-441_V6.5, operated at 700°C for 1050 h.
- C.3: IS1-437_V6.1, operated at 900°C for 650 h.

The initial characterization revealed only minor deviations in ohmic and polarization resistances. The ohmic resistances of the three cells were 1.570, 1.428, and 1.434 Ωcm^2 , respectively. The polarization resistances were 0.220, 0.195, and 0.200 Ωcm^2 , indicating comparable initial microstructures across all samples. Accordingly, microstructural differences revealed in post-test analyses can be attributed to changes occurring during testing.

Reference measurements were performed approximately every few hundred hours during operation. The resulting impedance spectra and DRTs for cells C.2 and C.3 are presented in Figures 4.33 and 4.34, providing a detailed comparison of the aging behavior of the infiltrated electrode systems at different temperatures.

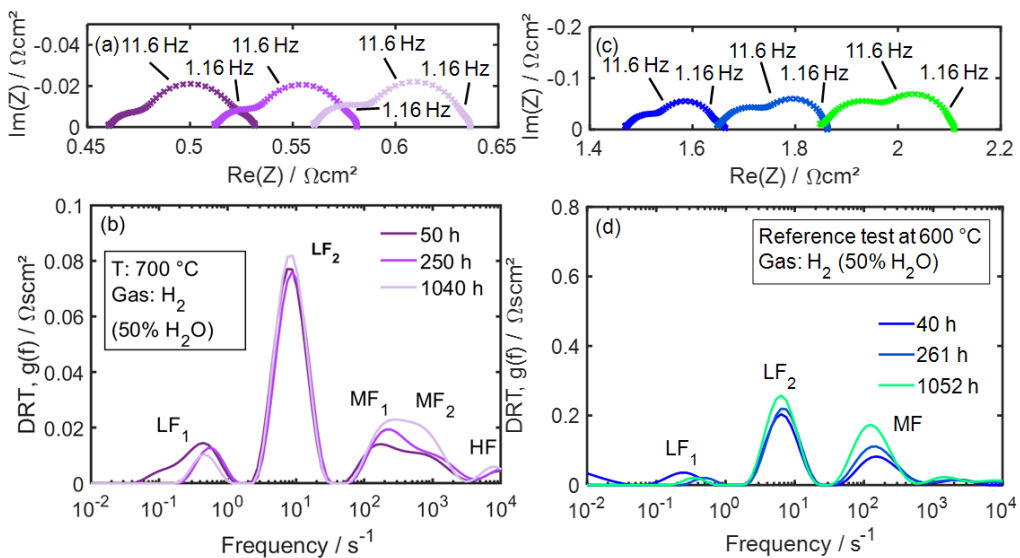


Figure 4.33: Time evolution of (a) impedance spectra and (b) corresponding DRTs of the electrode of cell IS1-441_V6.5 operated at 700 °C under a 50:50 steam/H₂ gas mixture. Time evolution of (c) reference impedance spectra and (d) corresponding DRTs. Adapted from (4).

During 1,100 h of operation at 700 °C, the gas diffusion peak LF₁ decreased between 50 and 250 h (Figure 4.33(b)), likely due to coarsening of fine GDC particles and subsequent enlargement of the pore structure (0.18 to 0.19 μm). Surface process LF₂ exhibited only minor changes over time, while the middle frequency peaks increased more significantly. Due to strong overlap between MF₁ and MF₂, it is not possible to determine which process contributes more to the observed degradation. Reference measurements at 600 °C confirmed similar trends for LF₁ and LF₂, as shown in Figure 4.33(c, d). In the DRT, the two middle frequency processes overlap as a single peak (Figure 4.33(d)), contributing to the largest increase in polarization resistance. Only minor

electrode changes are expected in C.2 based on the evolution of LF_2 as an indicator of electrode degradation.

Figure 4.34 shows the impedance evolution of electrode C.3 during operation at 900 °C, which differs from that of C.2 at 700 °C. The gas diffusion process LF_1 increased between 49 and 73 h (Figure 4.34(b)), possibly due to pore closure at high temperature, such as densification of the extra GDC layer on top of the Ni/GDC electrode. Afterwards, LF_1 decreased, resembling the trend observed in Figure 4.33(b). MF_1 increased steadily over time, while MF_2 showed a smaller increase. The contribution of LF_2 to polarization resistance initially increased (area under the peak at 73 h larger than at 49 h in the DRT) and then continuously decreased until 673 h. By the end of the test, LF_2 contributed less than its original value. The initial increase may be related to electrode degradation due to Ni agglomeration, GDC particle coarsening, and corresponding losses in TPB and DPB (Figure 4.36(c, d)). The subsequent decrease of LF_2 between 73 and 673 h remains uninterpretable. A similar “improvement” was observed in Section 4.4.1.1 and attributed to possible activation of the porous GDC interlayer by diffusion of nano-Ni particles. However, in cell C.3, the dense GDC interlayer (similar to Figure 4.14) likely inhibits Ni diffusion, making this mechanism unlikely. Overall, the complex impedance behavior recorded at 900 °C suggests that highly complex and/or time-dependent, inhomogeneous structural changes may have occurred within the electrode, which would not be expected at the nominal operating temperature of 600 °C.

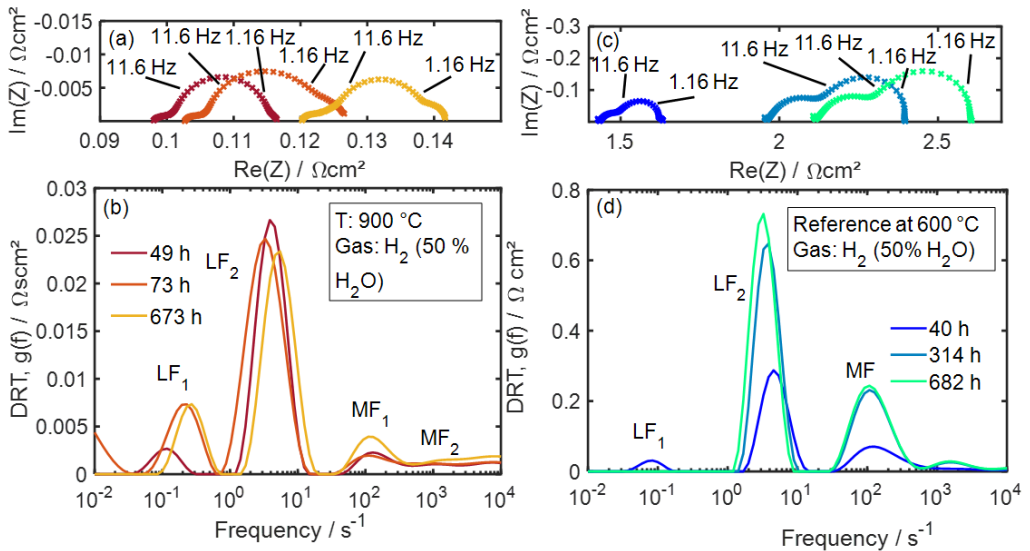


Figure 4.34: Time evolution of (a) impedance spectra and (b) corresponding DRTs of the electrode of cell IS1-437_V6.1 operated at 900 °C under a 50:50 steam/H₂ gas mixture. Time evolution of (d) reference impedance spectra and (e) corresponding DRTs. Adapted from (4).

Reference measurements performed at 600 °C, presented in Figure 4.34(c, d), show clear thermally activated aging in the process LF_2 . Due to the lack of data around 73 h, it is not clear whether the improvement in the LF_2 peak is also visible at 600 °C. Overall, the contribution of this process to the polarization resistance at 600 °C increased significantly after operating at 900 °C for approximately 650 h. This discrepancy between 600 and 900 °C still exists after CNLS-Fit with 5 RQ elements, as shown in Figure 4.35 (line 19). The R_{LF_2} increased from 0.137 to 0.301 Ωcm^2 , indicating a 120% increase. In contrast, for C.2, this value increased from 0.102 to 0.121 Ωcm^2 , corresponding to an increase of 18.6%. In comparison, electrode C.3 aged five times faster over a shorter period.

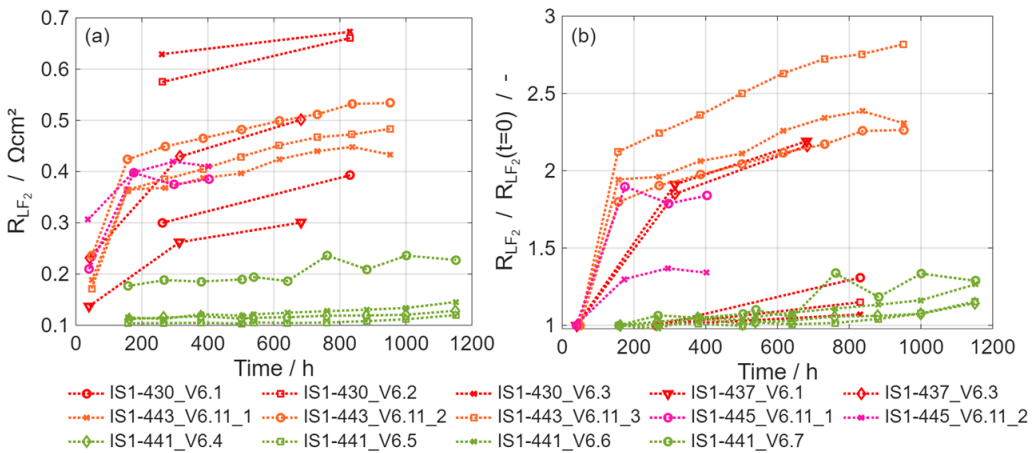


Figure 4.35: Time evolution of the fitted R_{LF_2} values of V6 cells listed in Table 4.3, shown as (a) absolute and (b) relative values. Cells No. 16–20 (IS1-430_V6.1, IS1-430_V6.2, IS1-430_V6.3, IS1-437_V6.1, and IS1-437_V6.3) were operated at 900 °C in humidified hydrogen (50% H_2O). Cells No. 21–23 (IS1-443_V6.11_1 to V6.11_3) were operated at 800 °C in humidified hydrogen (50% H_2O), whereas Cells No. 24–25 (IS1-445_V6.11_1 and IS1-445_V6.11_2) differed only in the humidity level and were operated at 10% H_2O . Cells No. 26–29 (IS1-441_V6.4, IS1-441_V6.5, IS1-441_V6.6, and IS1-441_V6.7) were operated at 700 °C in humidified hydrogen (50% H_2O).

Figures 4.14(a, b) and 4.36 present the SEM/BSE images of 3 tested cells. It is evident that the first two cells, C.1 (IS1-438_V6.5) and C.2 (IS1-441_V6.5), exhibit similar Ni tomography after testing, with GDC particles coarsening but remaining within 50 nm, thereby maintaining high TPB and DPB densities.

However, at 900 °C, a different phenomenon was observed. As illustrated in Figures 4.36(c, d), the sintering effect of the high temperature is apparent, with both the nanoscale GDC and Ni frameworks undergoing particle coarsening. Compared to results reported in (26), GDC growth is more pronounced than that of Ni particles. GDC phase coating of Ni surfaces occurred within less than 700 h. No Ni depletion was observed, likely due to operation under OCV without

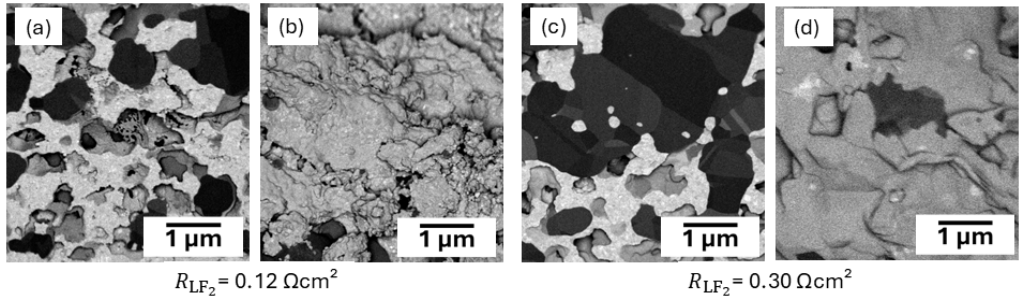


Figure 4.36: SEM/BSE images of polished and fractured cross-section of (a, b) cell C.2 (IS1-441_V6.5) and (c, d) C.3 (IS1-437_V6.1). Adapted from (4). The values for the LF₂ process are fitted from impedance under nominal conditions.

polarization. The resulting decrease in DPB and TPB densities is most likely responsible for the observed increase in polarization resistance. These assumptions are supported by the 3D reconstruction results, with the derived structural parameters listed in Table 4.7. The reconstruction and segmentation were carried out by Dr. Matthias Wieler from Bosch, Renningen. The further analysis was performed at IAM-ET, KIT.

Table 4.7: Microstructural parameters of cells C.1–C.3 derived via FIB-SEM.

Parameter/Cell	C.1, IS1-438_V6.5	C.2, IS1-441_V6.5	C.3, IS1-437_V6.1
$\varepsilon_{\text{pore}} / \%$	23	22	23
$\varepsilon_{\text{GDC}} / \%$	37	37	37
$\varepsilon_{\text{Ni}} / \%$	40	41	40
$l_{\text{TPB}} / \mu\text{m}^{-2}$	6.23	5.27	3.88
$A_{\text{Ni-Pore}} / \mu\text{m}^{-1}$	1.26	0.83	0.46
$A_{\text{GDC-Pore}} / \mu\text{m}^{-1}$	2.18	2.14	1.72
$\tau_{\text{Pore}} / -$	5.71	7.06	9.67
$\tau_{\text{GDC}} / -$	2.22	2.15	2.32
$\tau_{\text{Ni}} / -$	4.49	4.01	4.71
$d_{\text{pore}} / \mu\text{m}$	0.18	0.19	0.28
$d_{\text{GDC}} / \mu\text{m}$	0.32	0.30	0.32
$d_{\text{Ni}} / \mu\text{m}$	0.57	0.63	0.62
$r_{\text{ct}} / \cdot 10^{-5} \Omega\text{cm}^3$	1.80	2.50	9.62

The pristine cell exhibited the highest TPB density of $6.23 \mu\text{m}^{-2}$, which decreased by 15% to $5.27 \mu\text{m}^{-2}$ after operation at 700°C for 980 h (C.2). In the most aged cell C.3, the TPB density dropped to $3.88 \mu\text{m}^{-2}$, representing only 62.3% of the original value. A similar trend was

observed in DPB density, although with smaller relative changes: a 2% reduction for C.2 and 21% for C.3 compared to the pristine state. The Ni particles enlarged from 0.57 to 0.63 (+10.5% for C.2) and 0.62 (+8.8% for C.3) μm . The pore size increased from 0.18 to 0.19 μm after operating at 700 °C. This value increased to 0.28 μm after 650 h of operation at 900 °C. Surprisingly, no resolvable coarsening was observed in the GDC particles. One possible reason could be that the GDC particles in C.1 and C.2 are below the FIB-SEM's resolution limit.

These findings confirm that the GDC phase becomes structurally unstable at high temperatures, contributing to electrode reorganization. In contrast, it appears to be nearly stable at 700 °C, suggesting that the direct impact of its changes on aging at 600 °C is minimal. Thus, the test protocol for AST should be limited to the temperature range in which this phase remains structurally stable.

4.4.2.2 Cells from V6 at 900 °C and Lower

Several other V6 cells were operated between 700 °C and 900 °C. As their impedance evolution was comparable to that of cells C.2 and C.3, they are not discussed in detail but summarized in Table 4.3 and Figure 4.35. The figure illustrates thermally activated aging between 700 and 800/900 °C. Aging at 800 °C appears stronger than at 900 °C, likely due to the high mobility of the GDC phase and the resulting reorganization in the electrode observed for the latter case.

In test IS1-430, the R_{LF_2} values of all three cells increased during the two reference measurements at 600 °C, despite a continuous decrease observed at 900 °C. Due to the higher reduction temperature, cell IS1-430_V6.1 and IS1-430_V6.3 exhibited higher initial R_{LF_2} compared to their counterparts, IS1-437_V6.1 and IS1-437_V6.3, which had been reduced at 650 °C. With decreasing sintering temperatures, R_{LF_2} increased by 10% (IS1-430_V6.3), 18% (IS1-430_V6.2), and 35% (IS1-430_V6.1), which may be related to differences in electrode microstructure, with finer structures being more sensitive to degradation under this operating condition.

Cell IS1-437_V6.3 exhibited a larger initial R_{LF_2} due to its coarser structure. The R_{LF_2} increased from 0.23 Ωcm^2 to 0.43 Ωcm^2 (+87%) after 300 h, and further to 0.50 Ωcm^2 (+117%) over the next 350 h. Despite the larger absolute increase, the relative increase was comparable or slightly smaller than that of IS1-437_V6.1, indicating similar aging resistance.

Due to mechanical instability, impedance results of V6.11 cells under the same test conditions were inconsistent. Therefore, their R_{LF_2} from test IS1-443 and IS1-445 will not be discussed quantitatively. At 800 °C with 50% H_2O , all three V6.11 cells (IS1-443) showed a dramatic increase in R_{LF_2} for the first 150 h (>75%), followed by a further increase of 50% over the next

800 h. No electrode improvement was observed. Similar trends were observed for two cells operated at 10% H₂O in IS1-445.

Apart from cell IS1-441_V6.5, three other V6 cells were tested together. With increasing sintering temperature (IS1-441_V6.4 to IS1-441_V6.7), the initial R_{LF_2} generally increased, except for IS1-441_V6.4, likely due to poor Ni percolation. The LF₂ process showed similar degradation across all four cells, with increases of 20–30% after 1050 h.

The interlayer ensures mechanical integrity, allowing the Ni skeleton to sinter properly onto the structure. Direct sintering of Ni on the YSZ electrolyte leads to electrode delamination. Consequently, V6 cells are unsuitable for AST and the aging model.

4.4.3 Relationship between Structural Parameter and Charge-transfer resistance

Using the structural parameters and corresponding reference measurements, the r_{ct} can be determined via CNLS fitting based on the ECM shown in Figure 4.18. This was achieved by incorporating a TLM element into the All-Fit software according to Equations 2.68–2.70. A detailed description of parameter initialization is provided in Section 4.5.1. The fitting results are presented at the end of Tables 4.4, 4.5, 4.6, and 4.7. A physically based model linking the structural parameters to r_{ct} for the Ni/GDC electrode is not available, as Ni nanoparticles on the GDC surface could not be resolved. Consequently, a quantitative assessment of the DPB activity is not possible. Instead, a qualitative description of structural trends, in combination with r_{ct} , is provided here as a pre-study.

According to (193, 22), the growth of Ni particles follows a power function with an exponent of 0.2. Based on this assumption, the particle sizes were plotted against time, as shown in Figure 4.37 for operation at 900 °C and 800 °C. All particle sizes increased at 900 °C, with Ni showing the strongest growth (+110%). The tendency fits well with a power function, although this may be due to the limited number of data points. In contrast, the operation at 800 °C exhibited a smaller increase in particle size, particularly for GDC, which even showed a slight decrease.

At a lower reduction temperature, the TPB and DPB densities are both higher, indicating higher reaction activity, consistent with the measured impedance. This may be related to the mobility of the GDC phase. During reduction, the GDC can coat Ni particles, thereby suppressing their growth and reducing TPB and DPB. Thermally activated degradation is evident in TPB and DPB, as shown in Figure 4.37(b). The former decreased from 2.16 to 1.65 μm^{-2} (-24%) after 1100 h at 900 °C, while it dropped from 4.27 to 3.74 μm^{-2} (-12%) after 950 h at 800 °C. A similar trend

was observed for DPB. Because of improvements in polarization resistance and interlayer effects, directly relating the structural changes to the fitted r_{ct} is not meaningful.

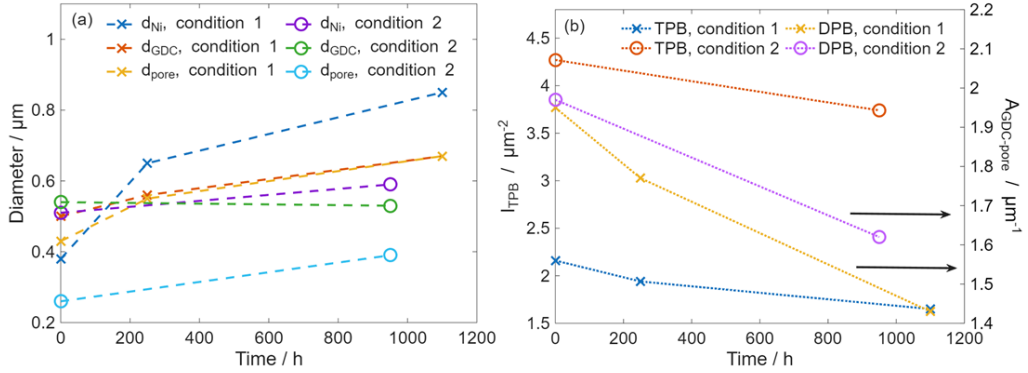


Figure 4.37: (a) Evolution of Ni, GDC, and pore diameter. (b) Evolution of TPB and DPB density. Condition 1: cells IS1-424_V1.2_1, IS1-429_V1.2_1, IS1-427_V1.2_1 reduced at 800 °C and operated at 900 °C with 50% fuel humidity. Condition 2: Cells IS1-442_V1.2, IS1-443_V1.2 reduced at 650 °C and operated at 800 °C (50% fuel humidity).

Due to differences in reconstruction and segmentation, the cells presented in Table 4.6 should be discussed separately. The Ni particle size clearly increased with time at 600 °C. A thermal-activated coarsening is observed at 700 °C. In contrast, the pore and GDC particles remained relatively stable. The fitted charge-transfer resistances are plotted against TPB and DPB in Figure 4.38(a, b), respectively. As TPB density increases, the r_{ct} decreases. A similar, but more linear, relationship is observed for DPB.

The cells from V6 (presented in Table 4.7) exhibit a similar decreasing trend of r_{ct} values with increasing TPB and DPB (Figure 4.38(c, d)). Moreover, they show a stable GDC phase, with constant particle size after 1050 h at 700 °C, despite their initially fine GDC structure. This suggests a structural change not resolvable by FIB/SEM.

4.4.4 Summary

This section summarizes the key electrochemical and structural degradation phenomena observed in the screen-printed and infiltrated cells under stress.

In screen-printed cells, aging behavior strongly depends on the test temperature. At 900 °C, cells from V1.2 exhibited a long-term improvement in polarization resistance despite clear structural degradation, including coarsening of Ni and GDC particles and reduced TPB/DPB densities. This apparent contradiction was attributed to possible surface diffusion of Ni into the GDC

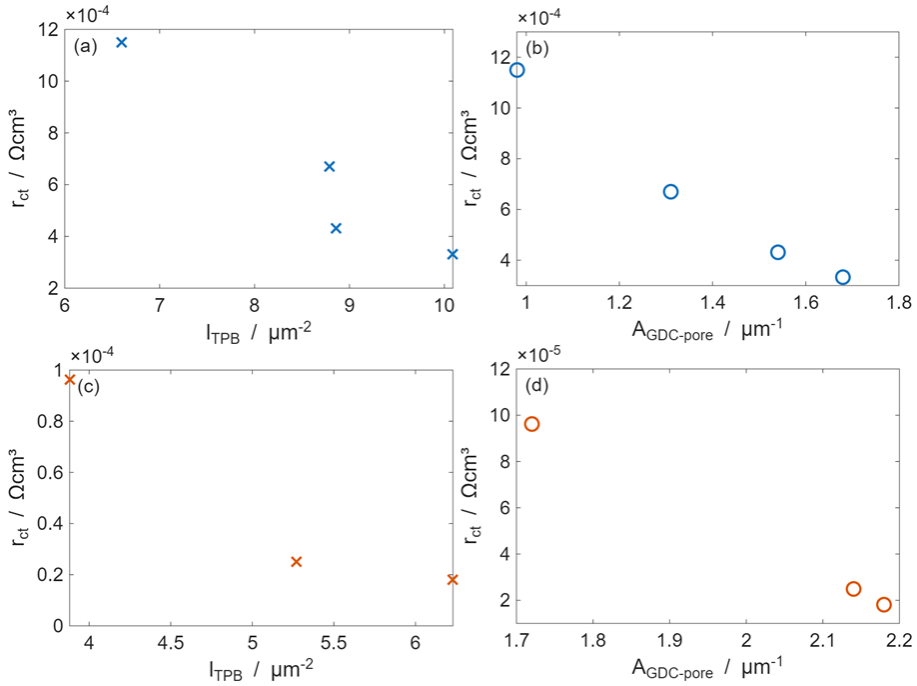


Figure 4.38: Relationship between fitted r_{ct} of cells from V1.2b (Table 4.6) to (a) TPB and (b) DPB. Relationship between fitted r_{ct} of cells from V6.5/V6.1 (Table 4.7) to (c) TPB and (d) DPB.

interlayer, which may have enhanced electrode activity. This hypothesis was validated with cell IS1-470_V1.5a without an interlayer operated at 900 °C, where only continuous aging, without improvement, was observed.

At 800 °C, the cell IS1-443_Ref1 displayed a sudden and severe degradation after an initial plateau. This behavior was attributed to chemical expansion in the GDC layer, amplified at elevated temperatures. In Ni/GDC electrodes, this effect is partially diluted by Ni, relieving internal stress. These findings suggest that operation at or above 800 °C introduces additional degradation mechanisms that are not dominant at nominal temperature and should therefore be avoided in ASTs.

Humidity also plays a significant role. At 800 °C, a lower H₂O content (10%) results in more pronounced improvement compared to 50% humidity, likely due to reduced gas-phase diffusion of Ni species and slower agglomeration. This behavior is also observed in test IS1-483 (Section 4.5.1), where the polarization resistance after restart is smaller than the value measured before cooling down. This may indicate a temporary regeneration mechanism in the Ni/GDC anode that could significantly affect durability testing under dynamic operating conditions.

At temperatures $\leq 750\text{ }^{\circ}\text{C}$, degradation occurred primarily in charge-transfer processes in the low-frequency region, correlating with microstructural changes such as particle coarsening and measurable decreases in TPB and DPB densities.

Infiltrated V6 variants exhibited excellent initial performance and similar temperature-dependent aging behavior as cells from V1.2. Above $750\text{ }^{\circ}\text{C}$, the GDC phase became highly mobile. This led to sintering effects, GDC coating on Ni, and loss of active interfaces. These effects complicated the interpretation of degradation mechanisms.

Based on these findings, cells without an interlayer and with clearly distinguishable LF and MF processes in their impedance spectra are most appropriate for aging studies. Among all tested variants, V1.5a demonstrated the best combination of electrochemical performance, interpretable impedance features, and suitability for post-test structural analysis. It was therefore selected as the reference cell for developing the aging model.

Other candidates were excluded for specific reasons:

- V6-variants were eliminated due to their complex structure, including a GDC interlayer required for mechanical stability and an additional GDC layer formed on top of the electrode during reduction.
- V3.12, V4.4, and V4.5 were excluded due to ultra-fine Ni networks, which hinder post-test analysis. HF processes dominated impedance responses and overshadowed degradation in electrode-relevant processes.

For the AST protocol, a maximum temperature of $750\text{ }^{\circ}\text{C}$ was decided to explore the upper limit of the suitable range. This threshold was intended to ensure the structural stability of the GDC phase, prevent electrode reorganization, and preserve the dominant aging mechanisms under nominal operating conditions.

4.5 Aging Behavior Analysis and Modeling

The results presented in this section are to be published in (7).

All the cells discussed in this section are from Variant V1.5a, which consists of an electrolyte, two screen-printed Ni/GDC layers sintered at $1300\text{ }^{\circ}\text{C}$, and two contact layers with a particle size of $0.5\text{ }\mu\text{m}$.

4.5.1 Comparison of Tested Cells

As described in Section 4.4, variant V1.5a was selected as the reference sample for the accelerated stress test (AST). The cells were reduced at 650 °C and subsequently operated at temperatures between 600 and 750 °C under humidified hydrogen containing 10–50% water vapor. Reference measurements were conducted at intervals of several hundred hours. The operating conditions and corresponding test durations are summarized in Table 4.8.

For clarity, the cells are numbered 1–9 in this section. Cells No. 1–6 correspond to tests performed at decreasing temperatures, whereas cells No. 6, 8, and 9 correspond to tests performed at decreasing humidity levels. Cell No. 7 represents the pristine cell. The use of the simplified numbering scheme (No. x) promotes readability compared with the original cell IDs, which consist of the test number and cell variant. Therefore, the cell numbering (No. x) together with the test number is used throughout this section in place of the cell IDs. The correspondence between the cell numbers, test numbers, and the original cell IDs is provided in Table A.11.

The pristine cell No.7, IS1-474, was analyzed using FIB-SEM. The sample preparation, reconstruction, and segmentation were carried out at LEM, KIT, by Dr. Ardavan Makvandi. The structural parameters were derived using in-house MATLAB® codes at IAM-ET, KIT, presented in Table 4.9.

Table 4.8: Operating conditions, test durations, corresponding ionic, electronic, and gas diffusion resistances, as well as the conversion factor F_c and its relative standard deviation for all nine tests.

No.	T [°C]	$p_{\text{H}_2\text{O}}$ [atm]	t [h]	R_{ion} [Ω/cm]	R_{el} [Ω/cm]	R_{diff} [$\cdot 10^{-3} \Omega \text{cm}^2$]	F_c -	STD/AVG -
1 IS1-471	750	50	450	62.4	12.3	4.79	9.30	0.73%
2 IS1-481	725	50	480	74.8	17.1	4.64	6.73	0.80%
3 IS1-469	700	50	550	124	28.6	4.49	4.75	1.80%
4 IS1-478	650	50	590	215	35	4.19	2.26	1.00%
5 IS1-483	625	50	2700	241	70	4.05	1.53	9.30%
6 IS1-479	600	50	1000	402	130	3.91	1.00	-
7 IS1-474	600	50	0	402	130	3.91	1.00	-
8 IS1-480	600	30	800	401	70	3.90	0.74	0.30%
9 IS1-475	600	10	780	395	45	7.34	0.62	1.20%

For all tested cells, two datasets were available: one measured at the elevated temperature (or varying humidity at 600 °C) and another at the nominal operating condition (600 °C, 50% H₂O

Table 4.9: Structural parameters of pristine cell No.7, IS1-474.

Parameter	ε_{GDC}	l_{TPB}	$A_{\text{GDC-Pore}}$	τ_{Pore}	τ_{GDC}	τ_{Ni}	d_{Pore}	d_{GDC}	d_{Ni}
Unit	%	μm^{-2}	μm^{-1}	—	—	—	μm	μm	μm
Cell No. 7	44.5	9.70	3.42	4.86	1.94	492	0.251	0.219	0.100

in hydrogen). Selected results from the former, comparing the BoL and the end of test (EoT), are presented in Figure 4.39. The exact timestamp of the latter can be found in Figure 4.42(b). Both datasets exhibited degradation in the polarization resistance, with no temporary improvement observed.

Among the four visible processes in Figure 4.39, the LF_2 process showed the strongest degradation, with the peak shifting toward lower frequencies. This was followed by an increase in the HF process, which was unrelated to the electrode. The two middle-frequency processes (MF_1 and MF_2) showed only minor increases. Based on simulations using the transmission line model in Simulink (Appendix A.1), the increment in MF_1 could be partly attributed to increasing charge-transfer resistance and the resulting increase in penetration depth (active volume), leading to increased transport losses in the GDC phase rather than to degradation of its ionic conductivity. Consequently, the r_{ct} extracted from the raw impedance data best captures the overall degradation trend across both low- and middle-frequency processes and was therefore selected as the primary degradation indicator.

According to Table 4.5, the cell IS1-443_V1.2b, operated at 800 °C for 950 h, exhibits an increase in tortuosity from 2.87 to 3.52. This corresponds to an 18% decrease in conductivity, i.e., an approximately 22% increase in both R_{ion} and R_{el} . In contrast, the cell IS1-441_V6.5, operated at 700 °C for 1000 h, shows a markedly smaller change (-3%), despite its initially ultrafine GDC microstructure, for which greater microstructural evolution would be expected. Therefore, it can be assumed that at temperatures below 700 °C, changes in GDC tortuosity and the corresponding ionic and electronic conductivities remain within $\pm 10\%$. These variations result in a maximum change in the fitted r_{ct} of 1.29% at 600 °C, 3.4% at 650 °C, and 2.3% at 700 °C. Even for the extreme case of a 22% change observed at 800 °C, the resulting variation in r_{ct} remains below 7.2%, within an acceptable error range. The minor change of the GDC phase in the cells listed in Table 4.8 can be seen in SEM images in Figure 4.40.

Considering both the negligible changes in GDC and their limited influence on the fitted r_{ct} , the ionic and electronic conductivities (and corresponding resistances) can be regarded as constant over the tests summarized in Table 4.8.

The next step is CNLS fitting using the equivalent circuit model in Figure 4.18. Several assumptions were made before parameter initialization:

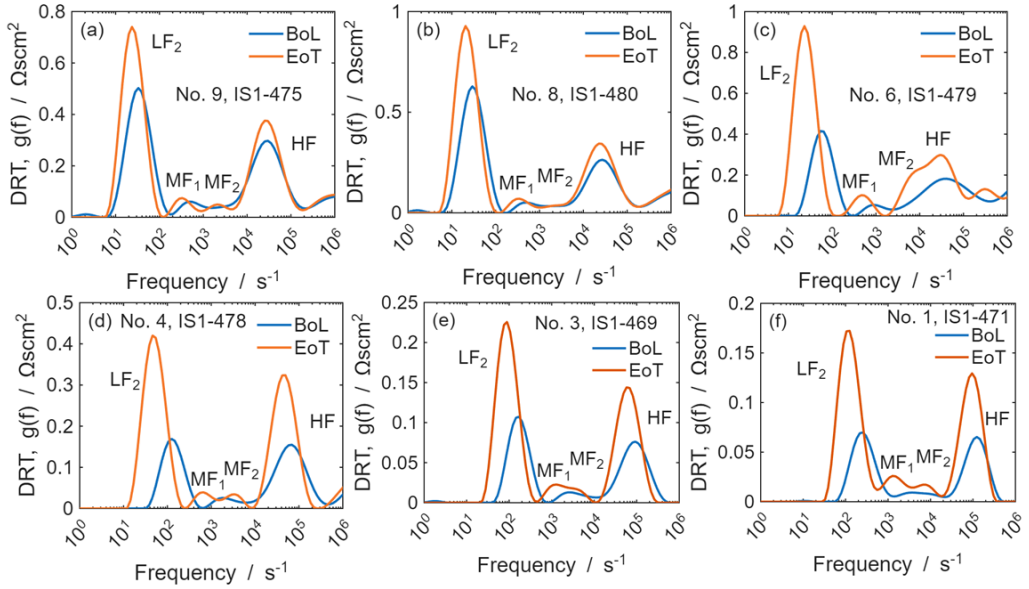


Figure 4.39: The DRTs of the impedance of electrodes from the following cells: (a) No. 9, IS1-475; (b) No. 8, IS1-480; (c) No. 6, IS1-479; (d) No. 4, IS1-478; (e) No. 3, IS1-469; and (f) No. 1, IS1-471. The corresponding test conditions are presented in Table 4.8. Adapted from (7).

- The electrode layer thickness is $8\text{ }\mu\text{m}$ for nine cells. This value was derived from SEM analysis of cell No. 7.
- The volume fraction of GDC in the electrode is constant (44.5%).
- The GDC microstructure remains approximately unchanged at $\leq 750\text{ }^{\circ}\text{C}$. Thus, tortuosity is assumed constant and equal to that of the pristine cell.
- All cells share the same diffusion geometry throughout the entire operation duration in the flow field and Ni mesh, which accounts for the most gas diffusion loss due to their thickness. Therefore, the diffusion resistance calculated from a single inert-gas alternating test is assumed to apply to all.
- Knudsen diffusion is neglected due to the pore size of the nickel mesh, which is on the order of several hundred μm . In this case, only the molecular diffusion coefficients of the respective species are calculated.

For parameter initialization, the gas diffusion loss was overshadowed by the LF_2 peak in variant V1.5a, as stated in Figure 4.16. According to (86), the characteristic diffusion length $L_{\text{Diff,EL}}$ of the fuel electrode is unknown. Therefore, the ratio of the microstructural parameter Ψ_{EL} to the

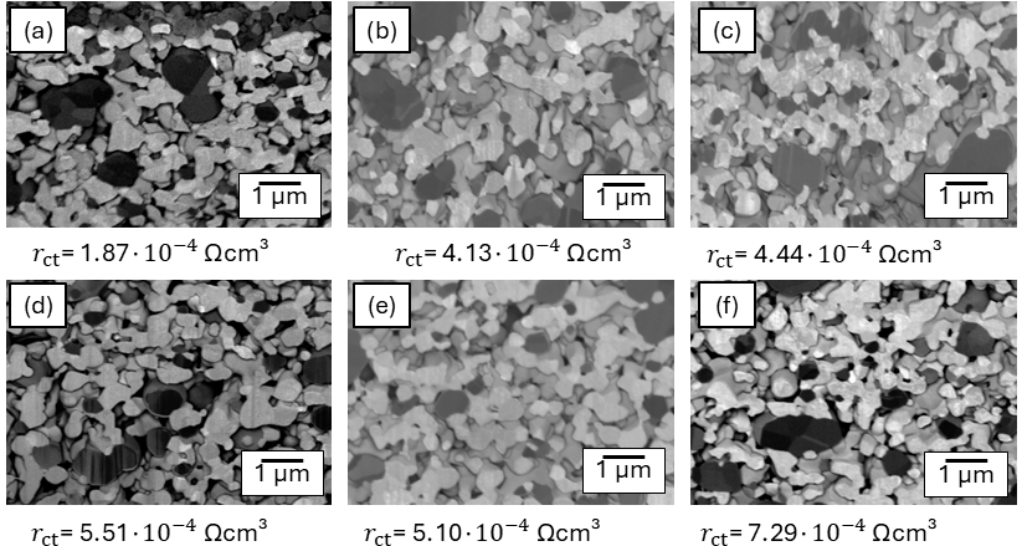


Figure 4.40: SEM/BSE cross-section images of electrodes from the following cells: (a) No. 7, IS1-474; (b) No. 6, IS1-479; (c) No. 4, IS1-478; (d) No. 3, IS1-469; (e) No. 2, IS1-481; and (f) No. 1, IS1-471. The r_{ct} was obtained by fitting the reference measurement at the end of testing based on the ECM shown in Figure 4.18, using the structural parameters of cell No. 7 (IS1-474_V1.5a) taken from Table 4.9. Adapted from (7).

characteristic diffusion length $L_{\text{Diff,EL}}$ is combined into a single parameter in Equation 4.17 and defined as the geometry factor of the fuel electrode.

$$G_{\text{EL}} = \frac{\Psi_{\text{EL}}}{L_{\text{Diff,EL}}} \quad (4.17)$$

The resistance change induced by alternating inert gas is $0.01 \Omega \text{cm}^2$, shown in Figure 4.16(d). The geometry factor is calculated to be 1380 based on the following Equation (86):

$$G_{\text{EL}} = \frac{\Psi_{\text{EL}}}{L_{\text{Diff,EL}}} = \left(\frac{R_g T}{2F} \right)^2 \cdot \frac{1}{\Delta R_{\text{Diff,EL}}} \cdot \frac{1}{P_{\text{cor}}} \cdot \dots \cdot \left\{ \left[\frac{1}{D_{\text{mol,H}_2} \cdot p_{\text{H}_2,\text{EL}}} + \frac{1}{D_{\text{mol,H}_2\text{O}} \cdot p_{\text{H}_2\text{O,EL}}} \right]_{\text{N}_2} - \left[\frac{1}{D_{\text{mol,H}_2} \cdot p_{\text{H}_2,\text{EL}}} + \frac{1}{D_{\text{mol,H}_2\text{O}} \cdot p_{\text{H}_2\text{O,EL}}} \right]_{\text{He}} \right\} \quad (4.18)$$

Based on Equations 2.20–2.24 and 2.31, the diffusion resistances for all nine cells regarding their applied operating conditions were calculated and are presented in Table 4.8. All necessary

material-specific values, such as the collision integral Ω_D and the Lennard-Jones characteristic length σ_{ij} , can be found in (86). The calculated value was fixed for the R in the RQ-element. The n parameter was set between 0.6 and 1, and the frequency range was aligned with that of the LF_2 peak.

Based on 3D reconstruction results, the tortuosity and volume fraction of GDC in the pristine cell are 1.94 and 44.5%, respectively. The intrinsic electronic and ionic conductivities of the 10GDC can be obtained from (77). The corresponding resistances applied in the TLM are calculated based on Equation 2.71 and 2.72 and listed in Table 4.8. These values can be applied to the entire dataset, as the GDC phase was presumed stable or its impact on the fit results is less than 7.5%. The remaining parameters, namely the charge-transfer resistance r_{ct} and the chemical capacitance of the electrode C_{ct} , are determined by fitting.

The two remaining RQ elements, representing the MF_2 and HF processes, are likely not part of charge-transfer processes. Therefore, no strict constraints were imposed, except that the n parameter was set to values between 0.6 and 1, and the frequency ranges were adjusted according to the corresponding DRTs.

The ohmic resistance is represented with a simple R-element, which is not discussed in this work.

Figure 4.41 presents a representative CNLS-fit result of cell No. 5 (IS1-483). The Nyquist plot in Figure 4.41(a) shows an excellent match, with the fitted impedance overlapping the measurement almost perfectly. This level of agreement is not observed in the DRT shown in Figure 4.41(b). The HF peak shows very good agreement with the fitted peak. In contrast, the fitted LF_2 peak appears slightly narrower, higher, and sharper than the measured response. This discrepancy is most likely due to electrode inhomogeneity, i.e., deviations from ideal electrode behavior that the fitting model does not adequately capture. A similar mismatch is observed for the MF process.

Despite these limitations, the overall fit quality remains high. The relative residuals of both the real and imaginary impedance components remain below 2.5% across the entire frequency range, indicating excellent agreement. While these residuals reflect the numerical agreement between the model and the measurements, they do not directly represent the uncertainty of the fitted parameters due to parameter correlation and model simplifications. For well-resolved processes, such as the r_{ct} related LF_2 , the parameter uncertainty can be estimated to be on the order of a few times the relative impedance residual. The uncertainty of r_{ct} is therefore estimated to be approximately 3–7% (303, 221, 304, 93, 305).

Another source of uncertainty arises from the assumption that GDC conductivity remains unchanged. Following the presumed maximum of 10% increase in electronic and ionic resistance, the resulting maximum error is estimated to be under 3.4%. Considering both contributions, the

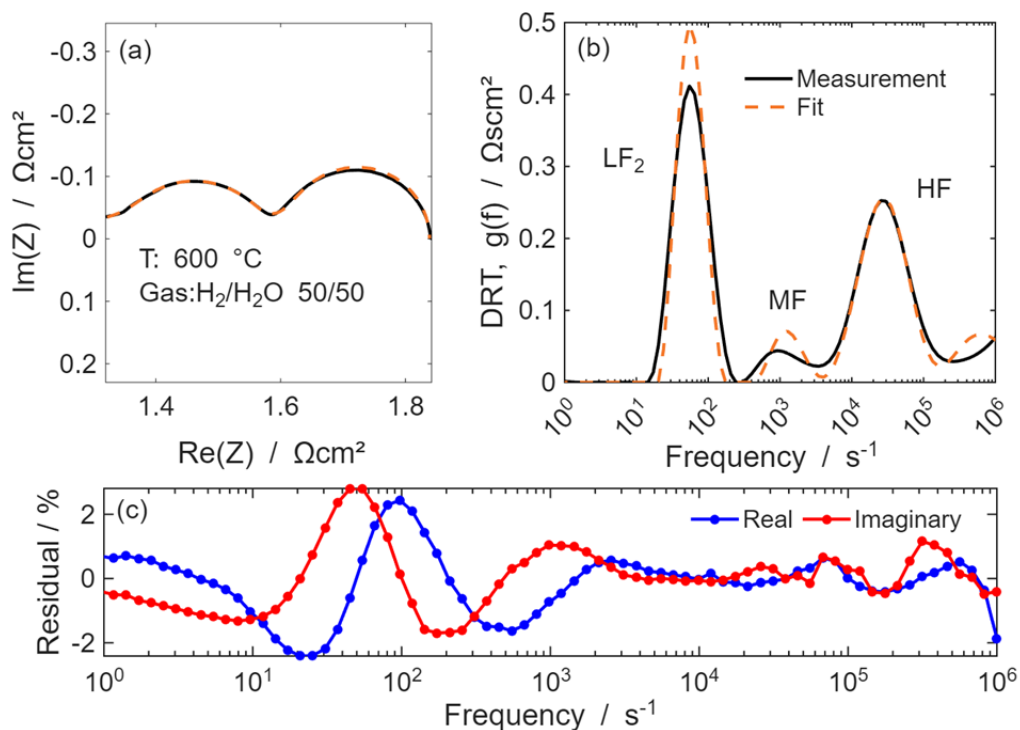


Figure 4.41: Fit results of the reference test for cell No. 5 (IS1-483), regarding (a) the Nyquist plot, (b) the DRT spectra, and (c) the real and imaginary residuals. Adapted from (7).

maximum overall uncertainty of the fitted r_{ct} can be estimated using the root-sum-of-squares approach:

$$\text{Overall error} \leq \sqrt{(7\%)^2 + (3.4\%)^2} \approx 7.8\%.$$

This level of uncertainty is within the expected range for CNLS fits of electrochemical impedance spectra with distributed electrode processes and minor inhomogeneities. In summary, the fit results are considered plausible under the chosen parameter initialization assumptions.

The fitted r_{ct} obtained from the durability tests and the corresponding reference measurements are plotted as a function of time in Figure 4.42. Figure 4.42(a) illustrates the raw data and the associated degradation trends under different operating conditions. The values vary substantially with temperature and humidity. Therefore, a direct comparison is not feasible.

A sudden increase in r_{ct} is observed for cell No. 8 (IS1-480_V1.5a) at approximately 190 h. This behavior may be related to a partial loss of active electrode area. Since the magnitude of this

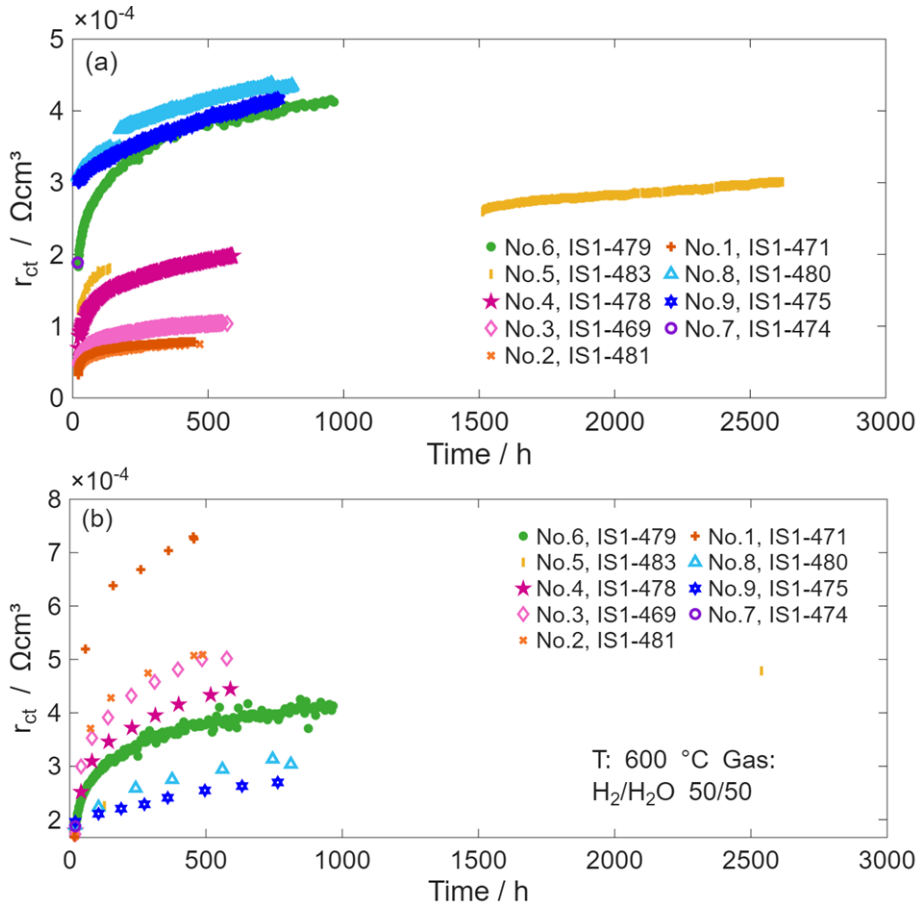


Figure 4.42: The time evolution of r_{ct} (a) at the elevated conditions and (b) of the reference measurements from cells 1-9. Adapted from (7).

jump is below 7.5 % and thus within an acceptable range, its influence is not considered in the subsequent data processing and modeling.

For cell No. 5 (IS1-483), a large data gap between 140 and 1490 h is present due to a communication failure between the Solartron and the test bench, which led to a restart for maintenance. Notably, the r_{ct} values during the first 20 h after the restart are lower than the last recorded value at 140 h. This apparent improvement is likely attributable to the intermediate cooling and reheating procedure, during which the cell was maintained in a dry atmosphere. Under these conditions, gas phase diffusion of Ni species is suppressed, whereas surface diffusion is enhanced, potentially leading to the formation of nanoscale Ni on the GDC surface. After adjustment of the humidity to 50 %, these nano-Ni particles rapidly transform into volatile Ni species and diffuse away.

Consequently, after 1,510 h, the degradation trend resumes the behavior observed before 140 h, suggesting a recovery of an electrode structure similar to that before cooling. Based on this observation, the data recorded between 1,490 and 1,510 h are excluded from Figure 4.42(a) and further analysis.

Figure 4.42(b) allows for direct comparison. The initial charge-transfer resistances ($r_{ct,ref}$) under nominal condition ranged from 1.69 to $1.97 \cdot 10^{-4} \Omega\text{cm}^2$, with an average of $1.80 \cdot 10^{-4} \Omega\text{cm}^2$ and a standard deviation of 7.4%. This narrow distribution indicates excellent reproducibility of the tested cells.

Taking cell No. 6 (continuous measurement at 600°C with 50% humidity) as the reference, clear thermally activated aging is observed, except for the data at 625°C . Due to a setup interruption, only two reference measurements before 1000 h were recorded, making this observation a possible singularity. Between 600 and 725°C , the temperature-accelerating effect of aging appears to weaken. The sudden increase between 725 - 750°C might indicate a change in the aging mechanism.

The tests performed at lower humidity (10% and 30% H_2O) at 600°C show that increasing humidity accelerates aging. After approximately 750 h, r_{ct} increased to $2.69 \cdot 10^{-4} \Omega\text{cm}^2$ for 10% humidity, to $3.13 \cdot 10^{-4} \Omega\text{cm}^2$ and $3.98 \cdot 10^{-4} \Omega\text{cm}^2$ for 30% and 50% humidity, respectively.

4.5.2 Data Processing Method

The content of this section is partially illustrated in (11).

Although direct comparison is possible using reference measurements, they are not suitable for subsequent aging modeling. Parameterization is strongly influenced by the number of data points. For example, with only three points, nearly any mathematical function can yield a good fit. Therefore, a novel data-processing method is developed to enable direct comparison using measurements recorded under elevated conditions. This method targets dataset standardization, transferring data acquired under stressed conditions to equivalent values at nominal conditions. An introduction to this approach is presented using the fitted r_{ct} of cell No. 3, IS1-469.

From the literature, r_{ct} represents the resistance associated with surface-related electrochemical processes, such as hydrogen adsorption/dissociation and electrochemical oxidation of H_2 (196, 238). Some of these processes are thermally activated. Hence, the resulting r_{ct} is expected to follow Arrhenius behavior. This implies that the relationship between the r_{ct} at 700°C and 600°C around one reference measurement (at around 42, 81, 140, 227, 311, 397, 484, 575 and 625 h, assuming negligible structural changes) can be expressed as:

$$\frac{r_{ct}(600\text{ }^{\circ}\text{C})}{r_{ct}(700\text{ }^{\circ}\text{C})} = \exp \left[-\frac{E_{a,ct}}{Rg} \left(\frac{1}{873\text{ K}} - \frac{1}{973\text{ K}} \right) \right] = \text{constant} = F_c \quad (4.19)$$

where $E_{a,ct}$ is the activation energy of the charge-transfer resistance and F_c is the conversion factor used to convert the fitted r_{ct} at 700 °C to the equivalent value at 600 °C for any time point:

$$r_{ct}(600\text{ }^{\circ}\text{C}) = F_c \cdot r_{ct}(700\text{ }^{\circ}\text{C}) \quad (4.20)$$

This approach is valid only if the reaction and aging mechanisms under accelerated conditions are identical to those under nominal conditions. On this basis, all time series data can be standardized to nominal conditions, enabling direct comparisons across cells and improving modeling reliability by increasing the number of data points. The conversion factor F_c is calculated using Equation 4.19, assuming that changes in the electrode between two adjacent measurements at 700 and 600 °C are negligible. To reduce error, F_c is calculated for every reference measurement and averaged. For cell No. 3, IS1-469, the factor was determined to be 4.68, with a standard deviation (STD) of 0.042 (9%), indicating a plausible standardization. The same method was applied to cells 1–6, and the conversion factors and $STD/AVGs$ are listed in Table 4.8.

Based on Equation 4.19 and the conversion factors at six different temperatures, the Arrhenius behavior of r_{ct} can be verified and its activation energy calculated. In Figure 4.43, $\ln(F_c)$ is plotted against $1/T$. The figure shows an excellent linear fit. From the slope of -13980 , an activation energy of 116.2 kJ/mol (1.20 eV) can be determined. This value is in good agreement with the literature value of 1.16 eV (196), confirming the reliability of the standardization process.

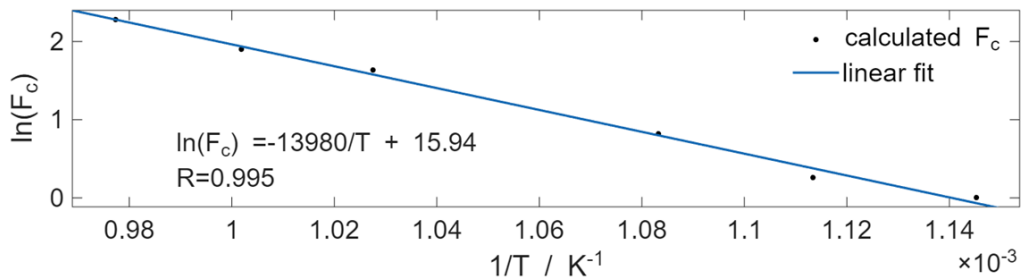


Figure 4.43: The linear relationship between $\ln(F_c)$ and $1/T$. Adapted from (7).

For cells No. 8, IS1-480 and 9, IS1-475, this method cannot be directly applied, as the dependency of r_{ct} on the partial pressures of hydrogen and steam differs. According to (196), a power-law dependence on both the hydrogen and steam partial pressures is assumed. Although the two

exponents a and b are unknown, a conversion factor F_c can still be calculated in analogy to Equation 4.19, as shown in Equation 4.21:

$$\frac{r_{ct}(50\%)}{r_{ct}(30\%)} = \frac{p_{H_2O,1}^a p_{H_2,1}^b}{p_{H_2O,2}^a p_{H_2,2}^b} = \frac{0.5^a \cdot 0.5^b}{0.3^a \cdot 0.7^b} = \text{constant} = F_c \quad (4.21)$$

As listed in Table 4.8, the standard deviation relative to the average (STD/AVG) is less than 1.2%, indicating excellent reliability. While only three humidity values were available, the fit of the power-law exponents was not performed.

The standardized r_{ct} are plotted against time and compared with the corresponding reference measurements in Figure 4.44, showing good agreement. Similar to Figure 4.42, thermally activated and humidity-enhanced aging is evident. However, the trends are now more clearly resolved. The only exception is cell No. 5 (IS1-483), for which the fitted r_{ct} values are approximately 3% lower than those of cell No. 6 (IS1-479) during the first 116 h. This deviation may be partly attributed to the smaller (-6.5%) initial r_{ct} , which was $1.69 \Omega\text{cm}^3$, compared to $1.80 \Omega\text{cm}^3$ for cell No. 6 (IS1-479). Although valid EIS results are unavailable after 116 h due to measurement failure, thermally activated aging is still expected to apply.

The data at 750°C show a sudden strengthening of aging. This indicates that additional aging mechanisms may be activated, such as sintering of the GDC phase observed at 900°C (Figure 4.36). Other possibilities include non-Arrhenius aging behavior, phase transitions in materials, or temperature-enhanced chemical expansion. In summary, aging modeling based on this dataset should be carried out with caution, as the dominant aging mechanism may differ from that under nominal conditions, and the use of the factor F_c is, in principle, not feasible.

With all time series datasets standardized, a consistent basis for inter-cell comparison has been established. The standardized r_{ct} , shown in Figure 4.44, now provides sufficient data density and comparability to enable robust modeling of aging behavior.

4.5.3 Model for Degradation Prediction

In this section, several mathematical approaches are introduced to describe the temporal evolution of r_{ct} . These methods are evaluated in terms of their reliability, underlying assumptions, and the validity of their predictions over different operating durations. The goal is to identify a modeling framework that accurately captures and describes the observed aging trends.

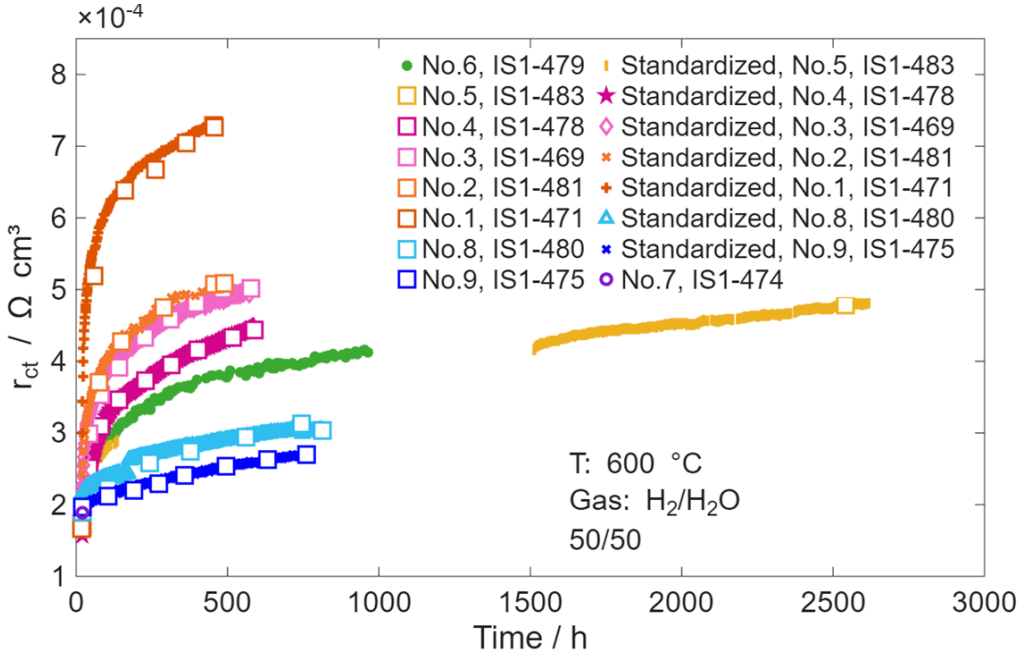


Figure 4.44: The time evolution of standardized r_{ct} of the cells 1-9 operated under different conditions compared to their reference measurements. The large square markers represent the reference measurements. Adapted from (7).

4.5.3.1 Arrhenius-Based Degradation Model

Since the tests on cells 1–6 varied only in operating temperature, an Arrhenius model is applied to examine whether a single thermally activated degradation mechanism can describe the aging behavior. This approach allows estimation of a temperature-dependent rate constant, which can be extrapolated to predict long-term performance at 600 °C.

Firstly, the validity of the assumption must be checked. With the degradation rate following Arrhenius behavior, the accumulated increase of r_{ct} as the integral of the degradation rate $k(t)$ over time t , also follows, with $E_{a,age}$ representing the activation energy of aging (21):

$$\frac{r_{ct} - r_{ct,ref}}{r_{ct,ref}} = \frac{\int k(t) dt}{r_{ct,ref}} \propto \exp\left(-\frac{E_{a,age}}{R_g T}\right) \quad (4.22)$$

The r_{ct} values of cells No. 1-6 were extracted from Figure 4.44 at five different time points. The reference $r_{ct,ref}$ is decided to be the average of the initial r_{ct} of cells 1-9, $1.80 \cdot 10^{-4} \Omega \text{ cm}^3$. The

differences $r_{\text{ct}} - r_{\text{ct,ref}}$ are listed in Table 4.10. The logarithms of $r_{\text{ct}} - r_{\text{ct,ref}}$ are plotted against $1/T$, as shown in Figure 4.45.

Table 4.10: Operating temperature of cells 1-6 and the relative changes of r_{ct} at 111, 150, 200, 300, and 450 h.

$T / ^\circ\text{C}$	Cell No.	$r_{\text{ct}} - r_{\text{ct,ref}}$					$/ \cdot 10^{-4} \Omega\text{cm}^3$
		111 h	150 h	200 h	300 h	450 h	
750	1 IS1-471	3.90	4.71	5.22	5.51	5.87	
725	2 IS1-481	1.59	2.22	2.59	2.97	3.23	
700	3 IS1-469	1.52	2.07	2.49	2.75	3.00	
650	4 IS1-478	0.814	1.49	1.84	2.12	2.41	
625	5 IS1-483	0.590	1.15	-	-	-	
600	6 IS1-479	0.634	1.09	1.48	1.69	1.97	
$E_{\text{a,age}} / \text{kJ/mol}$		63.8	45.2	34.3	33.5	29.2	
R_{fit}		0.920	0.975	0.984	0.996	0.998	

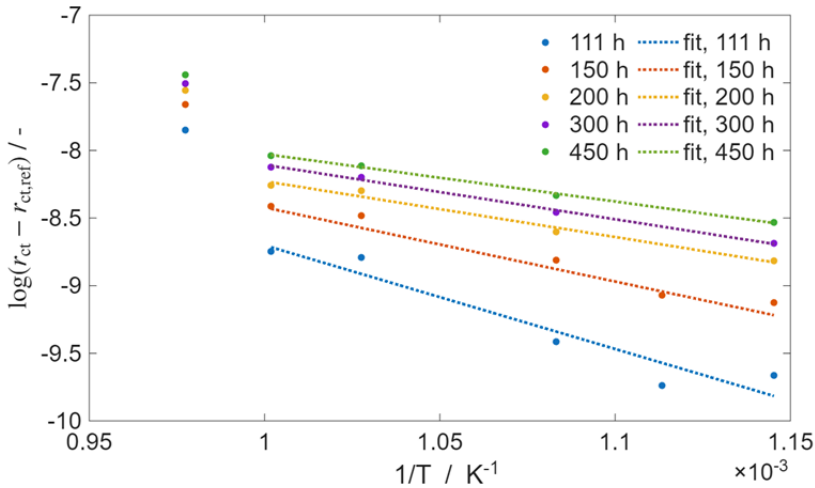


Figure 4.45: The logarithms of $r_{\text{ct}} - r_{\text{ct,ref}}$ of cell 1-6 plotted against $1/T$. Adapted from (7).

Figure 4.45 exhibits excellent linear behavior, excluding the points at 750 °C. The activation energy of aging is determined by a linear fit of the remaining points, as indicated by the dashed lines. The calculated activation energies and the corresponding fit robustness are listed in Table 4.10.

Along the time axis, an increasing R_{fit} is observed. This may be due to initial rapid processes, such as microstructural reorganization, that compete with the dominant aging mechanism in the long term. The calculated $E_{\text{a,age}}$ decreases over time, indicating a possible transition between different aging mechanisms. Within the first 200 h, $E_{\text{a,age}}$ drops quickly from 63.78 kJ/mol to 34.29 kJ/mol. In the subsequent 250 h, the value stabilizes around 29 kJ/mol. An additional calculation at 572 h yields an activation energy of 29.48 kJ/mol, in good agreement with the value at 450 h, suggesting that a stable dominant aging mechanism might have been established thereafter. Thus, 29.48 kJ/mol is determined to be the activation energy for aging.

As a result, a relatively linear aging behavior can be expected after 450 h. The r_{ct} between 450 h and 572 h for cell 6 can be calculated:

$$r_{\text{ct}}(600^\circ\text{C}, t) = 3.87 \cdot 10^{-4} \Omega\text{cm}^3 + A \cdot \exp\left(-\frac{29.48 \text{ kJ/mol}}{R_g \cdot 873.15 \text{ K}}\right) \cdot (t - 450 \text{ h})$$

Based on Figure 4.44, the degradation rate is calculated to be $6.42 \cdot 10^{-8} \Omega\text{cm}^3/\text{h}$. If this degradation mechanism continues to dominate until 100,000 h, the predicted r_{ct} values at 10,000 h and 100,000 h are:

$$\begin{aligned} r_{\text{ct}}(600^\circ\text{C}, 10,000 \text{ h}) &= 3.87 \cdot 10^{-4} + 6.42 \cdot 10^{-8} \cdot (10,000 - 450) \\ &= 1.00 \cdot 10^{-3} \Omega\text{cm}^3, \\ r_{\text{ct}}(600^\circ\text{C}, 100,000 \text{ h}) &= 3.87 \cdot 10^{-4} + 6.42 \cdot 10^{-8} \cdot (100,000 - 450) \\ &= 6.78 \cdot 10^{-3} \Omega\text{cm}^3. \end{aligned}$$

However, a decreasing aging rate, as observed in Ni/YSZ cells and described by a power law function (22), would invalidate this assumption. The predicted r_{ct} until 100,000 h is plotted in Figure 4.54 and compared to the predictions of other models.

For cells 8 and 9, the assumed Arrhenius-type degradation is not valid, as humidity affects the aging mechanism differently.

4.5.3.2 Power Function for Humidity

Humidity potentially influences the rate of r_{ct} increase in a non-Arrhenius manner. In the work of Ploner (21), the acceleration effect due to steam partial pressure is evaluated via a power law:

$$\frac{r_{\text{ct}, \text{pH}_2\text{O},1} - r_{\text{ct}, \text{ref}}}{r_{\text{ct}, \text{pH}_2\text{O},2} - r_{\text{ct}, \text{ref}}} = [\text{AF}(\text{steam})] = \left(\frac{p(\text{H}_2\text{O})_1}{p(\text{H}_2\text{O})_2} \right)^n \quad (4.23)$$

where n is the acceleration exponent, and $p_{\text{H}_2\text{O},2}$ and $p_{\text{H}_2\text{O},1}$ are the steam partial pressures under nominal and stressed conditions, respectively.

To determine the exponent n , the relative changes of r_{ct} at different time points were extracted, as listed in Table 4.11. The exponents n calculated for cells 8 and 9 are listed in Table 4.12

Table 4.11: The increase in r_{ct} of cells 6, 8 and 9 under different humidity conditions.

Humidity / %	$r_{\text{ct}} - r_{\text{ct}, \text{ref}}$						/ $\cdot 10^{-4} \Omega \text{cm}^3$
	111 h	150 h	200 h	300 h	450 h	600 h	760 h
50	0.634	1.090	1.480	1.690	1.970	2.010	2.080
30	0.480	0.600	0.790	0.930	1.100	1.230	1.390
10	0.200	0.280	0.360	0.460	0.600	0.700	0.800

Table 4.12: Acceleration exponent n derived from cell 8 and 9.

Time / h	111	150	200	300	450	600	760
$n(30\%)$	0.545	1.169	1.229	1.169	1.141	0.961	0.789
$n(10\%)$	2.259	2.661	2.767	2.547	2.327	2.065	1.871

As shown in Table 4.12, the exponent n varies significantly over time and differs between humidity levels. This indicates that the assumed power law relationship is not valid under the tested conditions. Consequently, no further discussion is given for this approach.

4.5.3.3 Aging Behavior Prediction Using Power Law Model

In Ni/GDC electrodes, degradation often slows over time due to microstructural stabilization and diffusion limitations. The power-law model is thus applied to test the hypothesis that r_{ct} exhibits sublinear time dependence, enabling more realistic long-term predictions than a purely linear increase. This approach assumes that r_{ct} increases with time in the form of:

$$r_{\text{ct}}(t, T, p_{\text{H}_2\text{O}}) = r_{\text{ct}, \text{ref}} + a \cdot t^n \quad (4.24)$$

where:

- a and n are temperature- and humidity-dependent fitting parameters,
- t is the operating time.

The model captures the slowing degradation rate typically observed in ceramic electrochemical systems after initial stabilization, as shown in Figure 4.44. The fit results and robustness are presented in Table 4.13.

Table 4.13: Power law fitting parameters and fit quality for r_{ct} at various temperatures and humidity levels.

$T / ^\circ\text{C}$	600	600	600	625	650	700	725	750
$p_{\text{H}_2\text{O}} / \text{atm}$	0.50	0.30	0.10	0.50	0.50	0.50	0.50	0.50
a	$2.60 \cdot 10^{-5}$	$1.09 \cdot 10^{-5}$	$1.92 \cdot 10^{-6}$	$1.83 \cdot 10^{-5}$	$3.44 \cdot 10^{-5}$	$6.15 \cdot 10^{-5}$	$7.55 \cdot 10^{-5}$	$1.94 \cdot 10^{-4}$
n	0.326	0.359	0.569	0.355	0.324	0.259	0.244	0.171
R_{fit}	0.983	0.972	0.993	0.999	0.972	0.993	0.997	0.990

Except at 625 °C, the parameter a shows a positive temperature dependence, while the exponent n exhibits an inverse tendency. Humidity appears to have a negative effect on n , and an increasing trend is observed for its impact on a . The standardized time series data, along with the corresponding power-law fits, as presented in Table 4.13, are shown in Figure 4.46. All time series were set to start at $t = 0$.

All fits show good agreement with the standardized data. However, the fit for cell No. 5 (IS1-483), which was operated at higher temperatures, lies below that of cell No. 6 (IS1-474), over the entire time scale. This behavior may be attributed to the absence of data between 114 and 1490 h. Consequently, the power-law fit primarily captures the aging behavior after 1490 h, whereas the fit for the other cell emphasizes faster degradation during the early aging phase. Because no cross-temperature physical constraint is imposed, long-term extrapolations may yield physically forbidden predictions inconsistent with thermally activated aging.

After 800 h, the fitted curve already begins to overestimate the r_{ct} of cell No. 6. Attempts to improve the fit by introducing an additional variable did not improve the fit quality. Instead, they resulted in poorer agreement with the data. This suggests that alternative models that can describe long-term aging with saturation behavior may be more appropriate. In the following section, a logarithmic fitting approach is therefore examined.

The predicted r_{ct} for nominal operating condition are $7.10 \cdot 10^{-4}$ and $1.29 \cdot 10^{-3} \Omega\text{cm}^3$ for 10,000 h and 100,000 h, respectively. These values are significantly smaller than those obtained

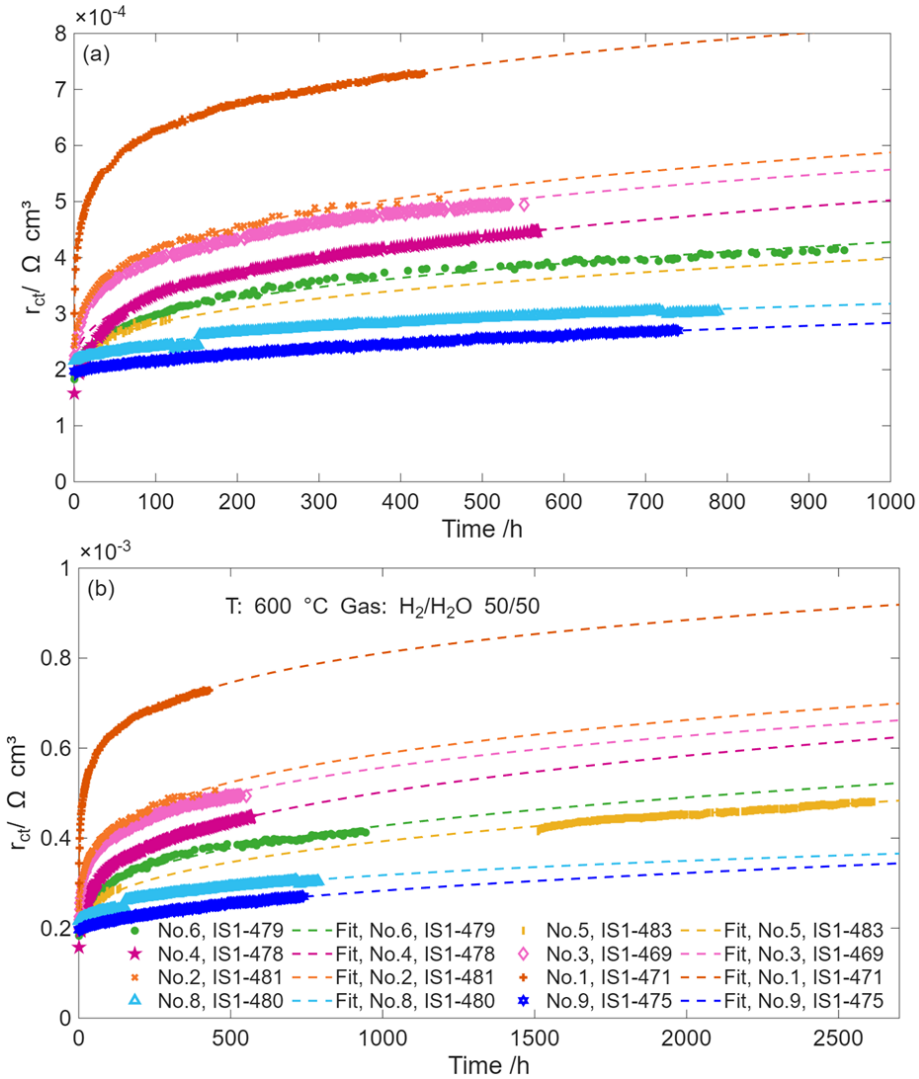


Figure 4.46: (a) Power-law fit results for cells No. 1–9 (excluding cell No. 7) over the first 1000 h. (b) Power-law fit results for cells No. 1–9 (excluding cell No. 7) over the first 2700 h. Adapted from (7).

from the Arrhenius degradation model, because the power-law approach assumes decelerating degradation.

This model can be applied to all datasets, since it is purely mathematical. However, it was observed that the choice of initial parameter values strongly influenced both the fit results and fit quality. In summary, without parameter restrictions grounded in physical principles, it is

difficult to obtain reliable results from a power-law fit with two free parameters. To address this limitation, a combination of the Arrhenius degradation and the power-law function is presented in Section 4.5.3.6.

4.5.3.4 Aging Behavior Prediction Using Logarithm Growth

A logarithmic time dependence is considered for assessing potential slowing of degradation over extended periods. The logarithm growth model is expressed as:

$$r_{\text{ct}}(t, T, p_{\text{H}_2\text{O}}) = r_{\text{ct,ref}} + a \cdot \ln(b \cdot t + 1) \quad (4.25)$$

This formulation reflects the assumption that degradation gradually decelerates and tends toward a quasi-saturated state. Such behavior has been reported in some electrochemical systems where early rapid changes are followed by slower, diffusion-limited, or interface-stabilized processes (306, 19, 195, 307).

The fit results are listed in Table 4.14 and presented in Figure 4.47. No clear dependency can be seen between the two parameters and humidity/temperature.

Table 4.14: Logarithms growth fitting parameters for r_{ct} at various temperatures and humidity levels.

$T / ^\circ\text{C}$	600	600	600	625	650	700	725	750
$p_{\text{H}_2\text{O}} / \text{atm}$	0.50	0.30	0.10	0.50	0.50	0.50	0.50	0.50
a	$5.34 \cdot 10^{-5}$	$2.91 \cdot 10^{-5}$	$3.413 \cdot 10^{-5}$	$9.44 \cdot 10^{-5}$	$7.04 \cdot 10^{-5}$	$5.84 \cdot 10^{-5}$	$5.43 \cdot 10^{-5}$	$6.90 \cdot 10^{-5}$
b	0.085	0.0898	0.161	0.0085	0.728	0.416	0.767	6.395
R_{fit}	0.997	0.997	0.999	0.999	0.989	0.981	0.999	1.00

Compared to the power-law model, the logarithmic model exhibits a slightly better fit. This is likely related to the pronounced early-stage degradation followed by a slower degradation, which is consistent with the functional form of a logarithmic model.

The fitting results show excellent agreement with the standardized data for all cells except cell No. 5 (operated at 625 °C). Although the dataset at 625 °C still exhibits apparently robust fitting, a substantial discrepancy is observed before 140 h. Most data points are located beyond 1510 h, where the aging rate is relatively mild but is given the highest weight in the fitting procedure. As illustrated in Figure 4.47(b), the curve for cell No. 5 lies below the fitted result for cell No. 6 before 1800 h. Thereafter, the two curves intersect, and the aging rate at 625 °C is predicted to be faster than that at 600 °C. This behavior highlights a limitation of independent mathematical modeling,

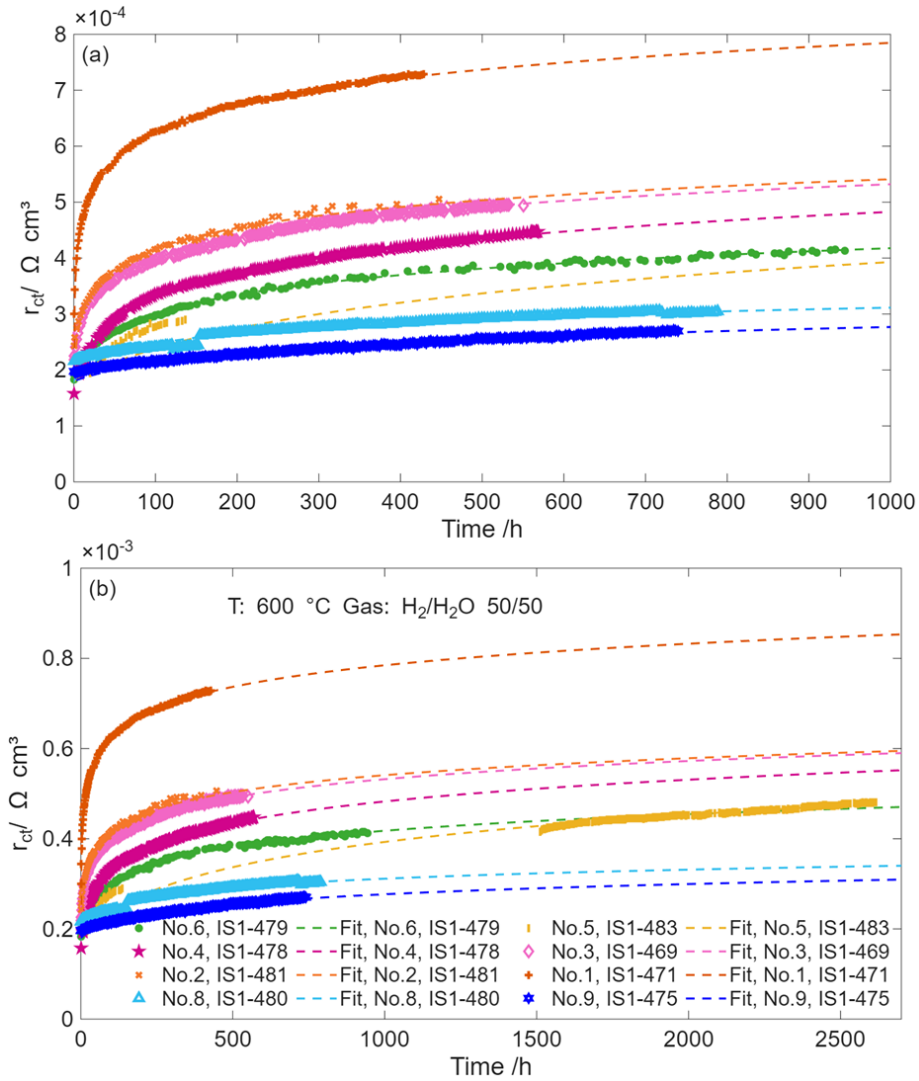


Figure 4.47: (a) Logarithm growth fit results for cells No. 1–9 (excluding cell No. 7) over the first 1000 h. (b) Logarithm growth fit results for cells No. 1–9 (excluding cell No. 7) over the first 2700 h. Adapted from (7).

as the resulting prediction could be partially physically forbidden. To address this limitation, a combination of the Arrhenius degradation and the logarithm growth function is presented in Section 4.5.3.8.

The predicted r_{ct} at 600 °C is $5.41 \cdot 10^{-4}$ and $6.63 \cdot 10^{-4} \text{ } \Omega\text{cm}^3$ for 10,000 h and 100,000 h, respectively. These values are much smaller than those predicted by the Arrhenius or power law methods.

Among the three models discussed (excluding the power-law model for humidity variation), the appropriate choice depends on the long-term aging behavior of the Ni/GDC electrodes. The Arrhenius-based model predicts a linear increase with time, whereas the power-law model captures degradation with a continuously decreasing rate. The latter tends to overestimate r_{ct} beyond approximately 800 h. Therefore, the actual degradation behavior is expected to lie below this prediction. In contrast, the logarithmic model represents an even milder degradation behavior that may approach saturation.

The exponential model introduced in Section 2.6.4 describes a true saturation in the aging tendency, which is not observed for all tested cells. Fitting attempts using this function failed to yield satisfactory solutions, indicating that the model cannot adequately describe the experimental data. In addition, attempts were made to combine the aforementioned mathematical functions. However, due to the presence of four free parameters and the absence of additional constraints, multiple parameter sets can produce comparably good fits, indicating the resulting aging description is ambiguous.

4.5.3.5 Equivalent Time Analysis

Instead of assuming a fixed mathematical function, the Equivalent Time Concept method uses empirical matching of equivalent aging states across different stress levels. This approach is applied to improve prediction robustness when multiple mechanisms or non-Arrhenius behavior are suspected.

Equivalent time analysis allows extrapolation from high-stress accelerated aging tests by identifying equivalent degradation states across different conditions (temperature, humidity, etc.) and mapping them to a common reference. Compared with conventional Arrhenius or power-law extrapolation, the method does not require an assumption about the functional form of degradation over time (section 2.6.5).

For each accelerated test condition, a set of degradation levels (20%, 50%, 80%, 100%, 110%, 125%, and 130% of increase in r_{ct}) is identified. The time required to reach each is determined and listed in Table 4.15 for varying temperatures.

The time durations required to reach specific degradation levels at elevated temperatures are compared against those at 600 °C, as presented in Figure 4.48(a, b). Several empirical relationships could be established with excellent fitting quality, including linear, polynomial, power, and

Table 4.15: Equivalent time data for operation under 50% humidity at different temperatures.

Cell No	$T / ^\circ\text{C}$	t / h to reach $\frac{r_{\text{ct}} - r_{\text{ct,ref}}}{r_{\text{ct,ref}}} / \%$						
		20	50	80	100	110	125	130
1 IS1-471	750	-	-	0.55	1.5	2.1	3.6	4.2
2 IS1-481	725	0.8	3	17	39	52	86	93
3 IS1-469	700	0.8	6	24	48	71	122	144
4 IS1-478	650	12	58	85	162	218	325	375
5 IS1-483	625	12	58	-	-	-	-	-
6 IS1-479	600	9	68	163	330	488	850	950

exponential-log functions. As only 2 data points are available at 625 °C (cell No. 5, IS1-483), this is insufficient to fit the aforementioned functions. The data of this cell are excluded from further analysis. The modeling approaches introduced in Sections 4.5.3.7 and 4.5.3.9 demonstrate linear and exponential–logarithmic trends, respectively, corresponding to Arrhenius-type degradation combined with power law and logarithm growth models. Therefore, they are not discussed here. The pure exponential function is excluded due to its unrealistically rapid increase.

The fitting results for the two remaining empirical (polynomial and power) functions are summarized in Table 4.16 and Figure 4.48(a, b). The excellent fit quality highlights a fundamental limitation of purely empirical modeling. Without physical justification, several functions can provide comparably good interpolation yet yield different results when extrapolated beyond the experimental range. Following the polynomial and power law functions, the standardized data at elevated temperatures were normalized/stretched to 600 °C, as illustrated in Figure 4.48(c-f).

Table 4.16: Function fitting results for equivalent time data at different temperatures with 50% humidity.

Transfer Function	750 °C	725 °C	700 °C	650 °C
$t_{600\text{ }^\circ\text{C}} = a \cdot t_{\text{elevated}}^2 + b \cdot t_{\text{elevated}} + c$	$a=4.382,$	$a=0.030,$	$a=-2.00 \cdot 10^{-3},$	$a=1.80 \cdot 10^{-3},$
	$b=202.3,$	$b=7.091,$	$b=6.937,$	$b=1.997,$
	$c=39.8,$	$c=25.4,$	$c=8.73,$	$c=-30.4,$
	$R_{\text{fit}}=0.997$	$R_{\text{fit}}=0.998$	$R_{\text{fit}}=0.998$	$R_{\text{fit}}=0.996$
$t_{600\text{ }^\circ\text{C}} = b \cdot t_{\text{elevated}}^a$	$a=0.961,$	$a=1.112,$	$a=0.956,$	$a=1.228,$
	$b=239.2,$	$b=6.038,$	$b=8.223,$	$b=0.656,$
	$R_{\text{fit}}=0.995$	$R_{\text{fit}}=0.996$	$R_{\text{fit}}=0.997$	$R_{\text{fit}}=0.996$

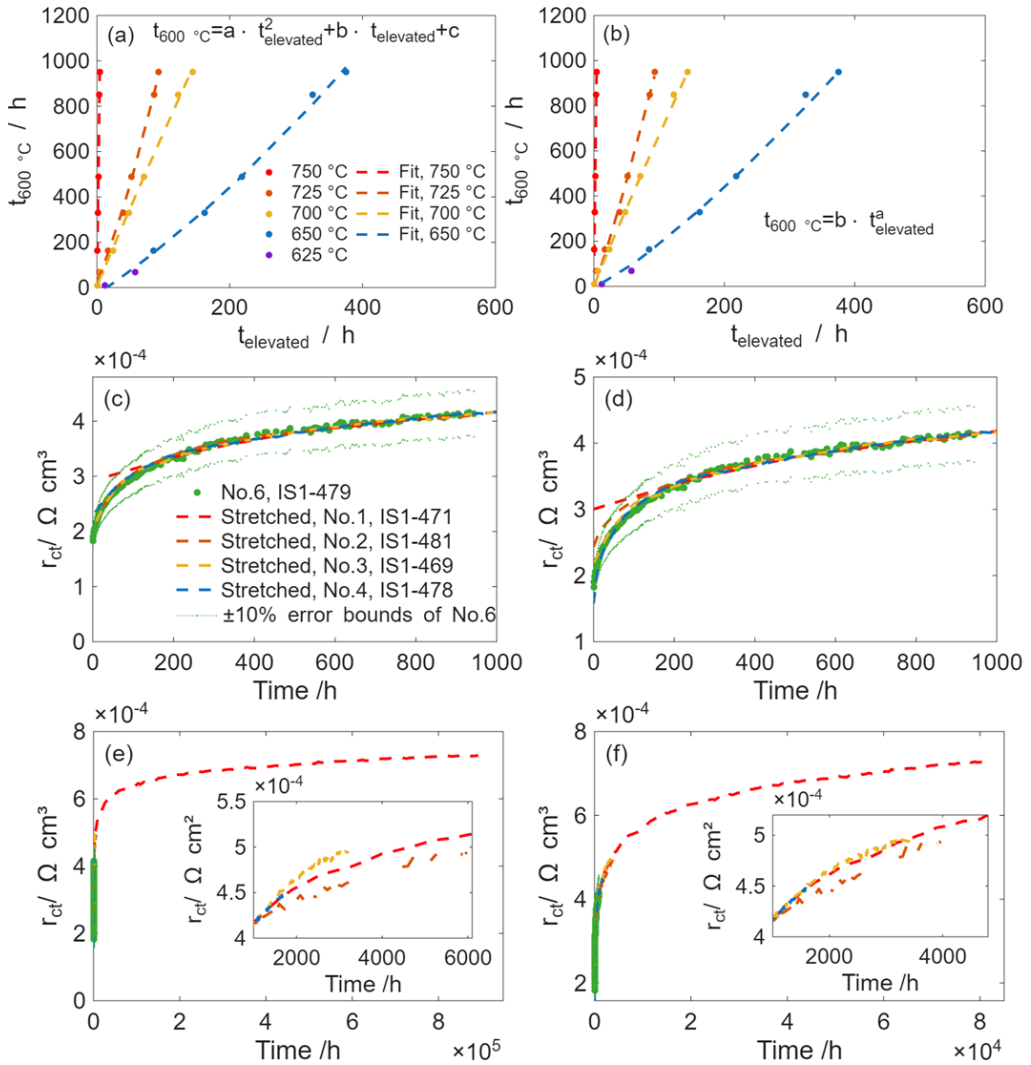


Figure 4.48: The (a) polynomial and (b) power function fit between $t_{600} \text{ } ^\circ\text{C}$ and t_{elevated} . The stretched r_{ct} -time data following the polynomial with parameters shown in Table 4.16 are presented in (c) within 1000 h and (e) within 900,000 h. The stretched r_{ct} -time data following the power function with parameters shown in Table 4.16 are presented in (d) within 1,000 h and (f) within 85,000 h. The zoomed-in windows emphasize the stretched data between 1,000–9,500 h for the polynomial and 1,000–5,500 h for the power function, respectively. The legend shown in (a) applies to (b). The legend in (c) applies to (c-f). Adapted from (7).

As indicated by the 10% error lines, the expanded data based on the polynomial function show excellent agreement with the measured data at 600 °C, except for the dataset at 750 °C before 100 h (Figure 4.48(c)). Similar observations are made for the power law function extrapolation

(Figure 4.48(d)). A possible explanation is the presence of a different dominant aging mechanism, as observed in section 4.5.3.1.

The stretched data in the temperature range of 650–725 °C allow predictions only up to approximately 5,981 h with the polynomial function and approximately 3,970 h with the power-law function. As shown in the zoomed-in views in Figure 4.48(e, f), the stretched datasets begin to diverge slightly by up to 5% up to 5,000 h for the former, whereas they maintain roughly an identical trend for the latter. Consequently, predictions extending to 100,000 h are not feasible with these approaches alone and should instead rely on or be combined with other degradation models.

Extrapolation from the 750 °C dataset, stretched using a polynomial function, is possible. However, due to the differences in underlying degradation mechanisms, the resulting predictions should be regarded as references only. Because the data for cell No. 1 (IS1-471) extend only to 80,958 h after stretching using the power-law function, only a lower bound can be obtained. The predicted r_{ct} at 10,000 and 100,000 h are summarized in Table 4.17.

Overall, these predicted values are smaller than those from the pure Arrhenius (linear) and power-law-based models, yet fall within a similar range to those predicted by the logarithmic growth model.

Table 4.17: Predicted r_{ct} at 600 °C based on equivalent time extrapolation using different empirical functions.

Transfer Function	r_{ct} at 10,000 h / Ωcm^3	r_{ct} at 100,000 h / Ωcm^3
$t_{600} = a \cdot t_{\text{elevated}}^2 + b \cdot t_{\text{elevated}} + c$	$5.43 \cdot 10^{-4}$	$6.42 \cdot 10^{-4}$
$t_{600} = b \cdot t_{\text{elevated}}^a$	$5.72 \cdot 10^{-4}$	$> 7.29 \cdot 10^{-4}$

Following the same procedure, the equivalent time concept can also be applied to humidity variations. Under this condition, the data obtained at higher humidity levels (30% and 50%) can be stretched to predict the degradation behavior at lower humidity (10%). Since the reference operating condition is 600 °C with 50% humidity, and operation at lower humidity is not typical, a detailed discussion of this case is not included in the present work.

4.5.3.6 Arrhenius Degradation with Power Function

As illustrated above, the single Arrhenius degradation model, pure mathematical functions, and the equivalent time concept each exhibit certain limitations. Specifically, the former alone cannot fully describe the degradation behavior; the middle is highly sensitive to initial parameters, and the latter lacks constraints on function selection, leading to multiple possible prediction outcomes.

Therefore, a combined Arrhenius–power-law model is introduced to simultaneously capture the thermally activated degradation and the decelerating trend over time.

The degradation rate k follows Arrhenius behavior. The time evolution of r_{ct} at a given temperature can be described by a power law function. Combining these two models, the degradation behavior can be expressed as:

$$r_{\text{ct}}(t, T) = r_{\text{ct,ref}} + a \exp\left(-\frac{E_{\text{a,age}}}{R_{\text{g}}T}\right)t^b \quad (4.26)$$

Choosing a certain aging level (e.g., 10%), the time required to reach this can be calculated via:

$$t = \left(\frac{0.1 r_{\text{ct,ref}}}{a \exp(-E_{\text{a,age}}/R_{\text{g}}T)}\right)^{1/b},$$

or in logarithm form:

$$\ln t = \frac{1}{b} \ln\left(\frac{0.1 r_{\text{ct,ref}}}{a}\right) + \frac{1}{b} \frac{E_{\text{a,age}}}{R_{\text{g}}} \frac{1}{T}.$$

Thus, the time required to reach the same level of degradation at different temperatures should follow Arrhenius behavior. The logarithm of time listed in Table 4.15 was plotted against $1/T$ for cells 1–6, as shown in Figure 4.49. The $\ln(t) - \frac{1}{T}$ plot shows good linearity except for the points at 750 °C, indicating a potential new dominant degradation mechanism. Excluding the 750 °C data, linear fit results are listed in Table 4.18. The linearity improves (i.e., larger R_{fit}) as the degradation level increases. A decrease in E_{a}/b is observed. After 80% degradation, the value stabilizes at 135.3 ± 0.6 kJ/mol, indicating that the Arrhenius assumption is valid once the initial aging, influenced by multiple competing mechanisms, is surpassed.

Table 4.18: Fitted parameter $1/b \cdot E_{\text{a,age}}$ for Equation 4.26.

Parameter	$(r_{\text{ct}} - r_{\text{ct,ref}})/r_{\text{ct,ref}}$						/ %
	20	50	110	80	100	125	130
$1/b \cdot E_{\text{a,age}} / \text{kJ/mol}$	179.0	196.7	137.3	131.5	134.7	135.3	135.8
$R_{\text{fit}} / -$	0.784	0.887	0.974	0.978	0.990	0.999	0.999

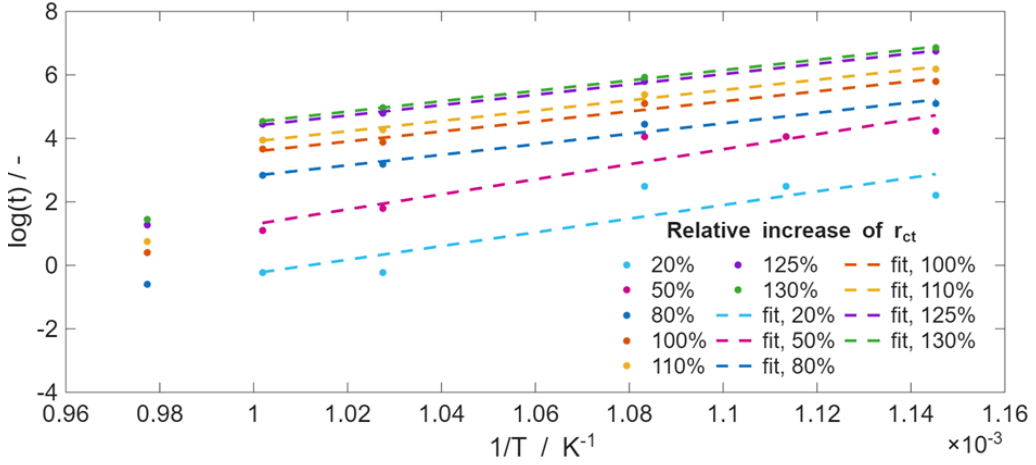


Figure 4.49: The logarithm of time required to reach a fixed degradation level plotted against $1/T$ for cells 1–6. Adapted from (7).

Direct fitting based on Equation (4.26) did not converge due to too many free parameters. A practical alternative is to adopt the average $E_{a,age}/b = 135.3$ kJ/mol obtained for degradation $\geq 80\%$. The Equation (4.26) is then transformed to:

$$r_{ct}(t, T) = 1.80 \cdot 10^{-4} \Omega\text{cm}^3 + a \exp\left(-\frac{135.3 \text{ kJ/mol} \cdot b}{8.314 \cdot T}\right) t^b, \quad (4.27)$$

reducing unknown parameters and emphasizing the phase in which a thermally activated mechanism dominates. The reformed equation is fitted using the standardized r_{ct} time series data from 600–725 °C. The fitted parameters are $a = 3.79 \cdot 10^{-3}$ and $b = 0.2437$. The corresponding activation energy for aging is 33.0 kJ/mol. The fit results and residuals are shown in Figure 4.50.

The coefficient of determination, $R_{fit} = 0.922$, indicates a good overall agreement between the fitted model and the experimental data. As shown in Figure 4.50(b), the residuals are large at the beginning of the test, showing a drastic decreasing trend afterwards. Among all, the data at 650 °C exhibit the largest deviation from the fit, followed by 600 °C, 700 °C, 725 °C, and 625 °C. The measured values are initially smaller than the fit, consistent with the calculated $1/b \cdot E_a$ being larger in the early stage, and using the stabilized value of 135.3 kJ/mol gives more weight to the long-term behavior. After 50 h, all residuals fall below 10%. Subsequently, the residuals remain within $\pm 5\%$, indicating excellent fit quality thereafter. The expression of evolution of r_{ct} at nominal condition is thus:

$$r_{ct}(t, 600 \text{ °C}) = 1.80 \cdot 10^{-4} + 4.035 \cdot 10^{-5} \cdot t^{0.2437} \Omega\text{cm}^3,$$

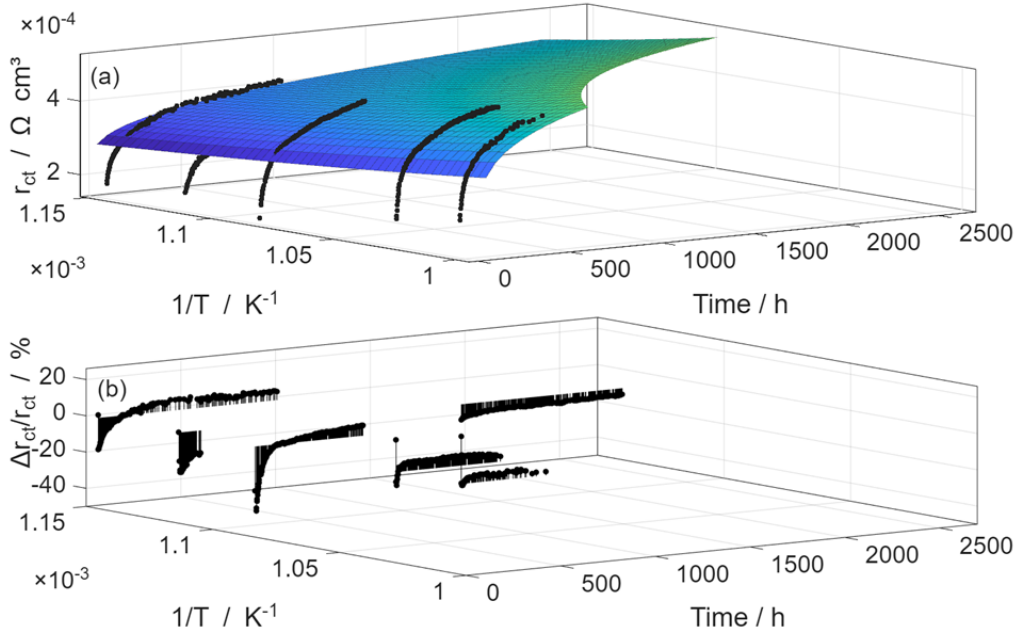


Figure 4.50: (a) The fit results of reformed Equation (4.26) from the standardized r_{ct} time series data from 600–725 °C. (b) The fit residues. Adapted from (7).

The predicted r_{ct} values for 10,000 h and 100,000 h are $5.61 \cdot 10^{-4}$ and $8.47 \cdot 10^{-4} \Omega\text{cm}^3$, respectively. From Figure 4.50(b), a slight underestimation (-5.24%) in fit values after 176 h is present.

4.5.3.7 Equivalent Time Concept Based on Arrhenius Degradation Behavior and Power Law

Further combination with the equivalent time concept is possible. The relationship between the time needed to reach a certain degradation level at T_{elevated} and at 600 °C is:

$$\ln \frac{t_{\text{elevated}}}{t_{600\text{ °C}}} = \frac{1}{b} \frac{E_{a,\text{age}}}{R_g} \left(\frac{1}{T_{\text{elevated}}} - \frac{1}{873.15\text{ K}} \right),$$

or equivalently:

$$t_{600\text{ °C}} = t_{\text{elevated}} \exp \left[\frac{-1}{b} \frac{E_{a,\text{age}}}{R_g} \left(\frac{1}{T_{\text{elevated}}} - \frac{1}{873.15\text{ K}} \right) \right].$$

Using the stabilized value $E_{a,age}/b = 135.3 \text{ kJ/mol}$ for the data acquired at 725°C for example:

$$\frac{t_{600^\circ\text{C}}}{t_{725^\circ\text{C}}} = \exp \left[\frac{-135.3 \text{ kJ/mol}}{R_g} \left(\frac{1}{998.15 \text{ K}} - \frac{1}{873.15 \text{ K}} \right) \right] \approx 10.32.$$

The time required to reach the same degradation level at 600°C is 10.32 times that at 725°C . Consequently, the dataset measured at 725°C could be stretched horizontally by a factor of 10.32. The result is shown in Figure 4.51(a), presented by orange "x" markers.

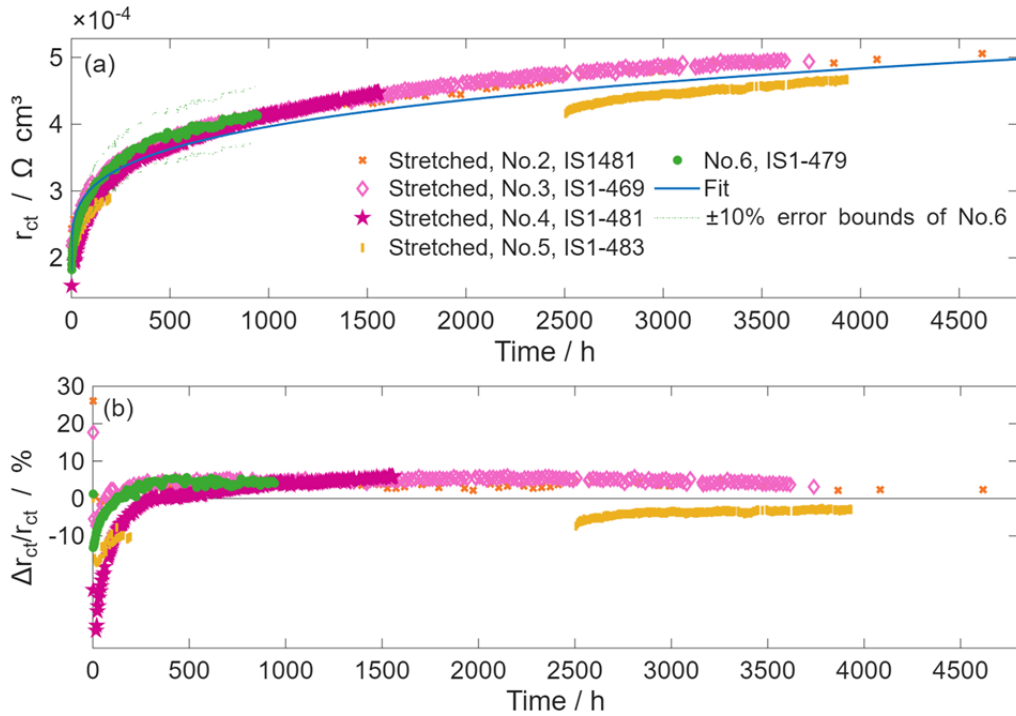


Figure 4.51: (a) The horizontally stretched r_{ct} -time datasets are compared to the data from 600°C and the fit result based on Equation 4.27. (b) The fit residues. Adapted from (7).

The same method was applied to the datasets measured at 625 – 700°C , yielding stretch factors of 1.68, 2.74, and 6.79, respectively. If the equivalent time concept, based on a purely linear relationship, is applied directly to the data in Table 4.15, the resulting stretch factors are 9.89, 6.65, 2.71, and 1.28 as temperature decreases. The deviations between the direct fit and the fit incorporating physical constraints are -4.2% , -2.0% , -1.0% , and -23.8% , respectively. Except for 625°C , all results agree well. The large deviation at 625°C is likely due to the limited data

size. Overall, the stretch factors calculated assuming Arrhenius-type degradation behavior are more physically plausible.

The corresponding stretched datasets are presented in Figure 4.51(a). The two thin green dashed lines indicate a $\pm 10\%$ deviation band with respect to the 600 °C dataset. Within the first 1000 h, the stretched data at 625 °C, 650 °C, 700 °C, and 725 °C remain within this band. Consequently, predictions derived directly from the stretched datasets can be considered plausible.

From the stretched data, the r_{ct} value at a maximum equivalent time of 4,617 h for 600 °C can be estimated. The stretched curves of cells No. 2–4 (650–725 °C) exhibit a generally consistent trend, whereas the curve of cell No. 5 (625 °C) is located slightly below the others. The resulting deviation is approximately 7.4%, which remains within an acceptable range. This deviation may be partially attributed to the slightly lower initial charge-transfer resistance of this cell.

To directly predict r_{ct} at 100,000 h, the 725 °C test would need to last at least 9,690 h, which is not feasible in the framework of this thesis. Long-term predictions must therefore be based on fitting using Equation 4.27.

The fitted values are $a = 3.788 \cdot 10^{-3}$ and $b = 0.244$. The corresponding activation energy for aging is 33.0 kJ/mol. Compared to the fit performed on the unstretched data, the values are very similar. The fit from the four stretched datasets, together with the original 600 °C data, and the corresponding residuals are shown in Figure 4.51.

During the first 150 h, residuals exceed -10%, with higher temperatures showing smaller deviations. Over 150 h, residuals rapidly decrease and remain within the $\pm 10\%$ range until 4,700 h. The initial 150 h likely correspond to a phase where multiple degradation mechanisms compete. The fit afterwards, which is essential for long-term prediction, shows excellent agreement. The expression of evolution of r_{ct} at nominal condition is thus:

$$r_{ct}(t, 600\text{ °C}) = 1.80 \cdot 10^{-4} + 4.012 \cdot 10^{-5} \cdot t^{0.244} \Omega\text{cm}^3,$$

The predicted r_{ct} values for 10,000 h and 100,000 h are $5.65 \cdot 10^{-4}$ and $8.45 \cdot 10^{-4} \Omega\text{cm}^3$, respectively. Compared to the models discussed in the last section, the further combination with the equivalent time concept yields slightly different values ($\pm 0.7\%$). This is because stretching the datasets to larger time scales places more weight on long-term aging behavior, reducing the influence of the early stage.

4.5.3.8 Arrhenius degradation with Logarithm Growth

In cases where degradation slows strongly over time, a logarithmic time dependence may be more appropriate than a power law. The evolution of r_{ct} can alternatively be described by a logarithmic function of the form:

$$r_{ct}(t, T) = r_{ct,ref} + a \cdot \exp\left(-\frac{E_{a,age}}{R_g T}\right) \cdot \ln(b \cdot t + 1) \quad (4.28)$$

This model accounts for the temperature-dependent acceleration of aging (Arrhenius behavior) as well as the commonly observed slowing down of degradation over time (logarithmic growth). Setting a certain aging level (e.g., 10%), the term $b \cdot t + 1$, consisting of the time t needed to reach it, can be calculated based on Equation 4.28:

$$b \cdot t + 1 = \exp\left(\frac{0.1 \cdot r_{ct,ref}}{a \cdot \exp\left(-\frac{E_{a,age}}{R_g T}\right)}\right) \quad (4.29)$$

Taking the logarithm:

$$\ln(b \cdot t + 1) = \frac{0.1 \cdot r_{ct,ref}}{a} \cdot \exp\left(\frac{E_{a,age}}{R_g T}\right) \implies \ln(\ln(b \cdot t + 1)) = \ln\left(\frac{0.1 \cdot r_{ct,ref}}{a}\right) + \frac{E_{a,age}}{R_g T}$$

Due to the unknown parameter b , the validity of the assumed Arrhenius degradation cannot be assessed by simple plotting but can only be evaluated after fitting the model parameters.

The standardized data at 600-725 °C were fitted using Equation 4.28. The fitted activation energy, $E_{a,age}$, is 38.5 kJ/mol. The corresponding coefficient was determined to be $a = 7.7 \cdot 10^{-3}$ and $b = 0.2251$. The fit results and associated residuals are shown in Figure 4.52(a, b). The coefficient of determination, R_{fit} , is 1.00, indicating excellent overall agreement.

As seen in Figure 4.52(b), the residuals are largest at the beginning of the tests and exhibit a sharp decreasing trend thereafter. Among all, the 725 °C dataset shows the largest deviation from the fit, followed by 700 °C, 625 °C, and 600 °C. After 50 h, all residuals fall below and remain within $\pm 10\%$, confirming excellent fit quality. However, a tendency to underestimate r_{ct} is already evident after 160 h at 600 °C, highlighting the limitations of this logarithmic growth-based model for long-term prediction.

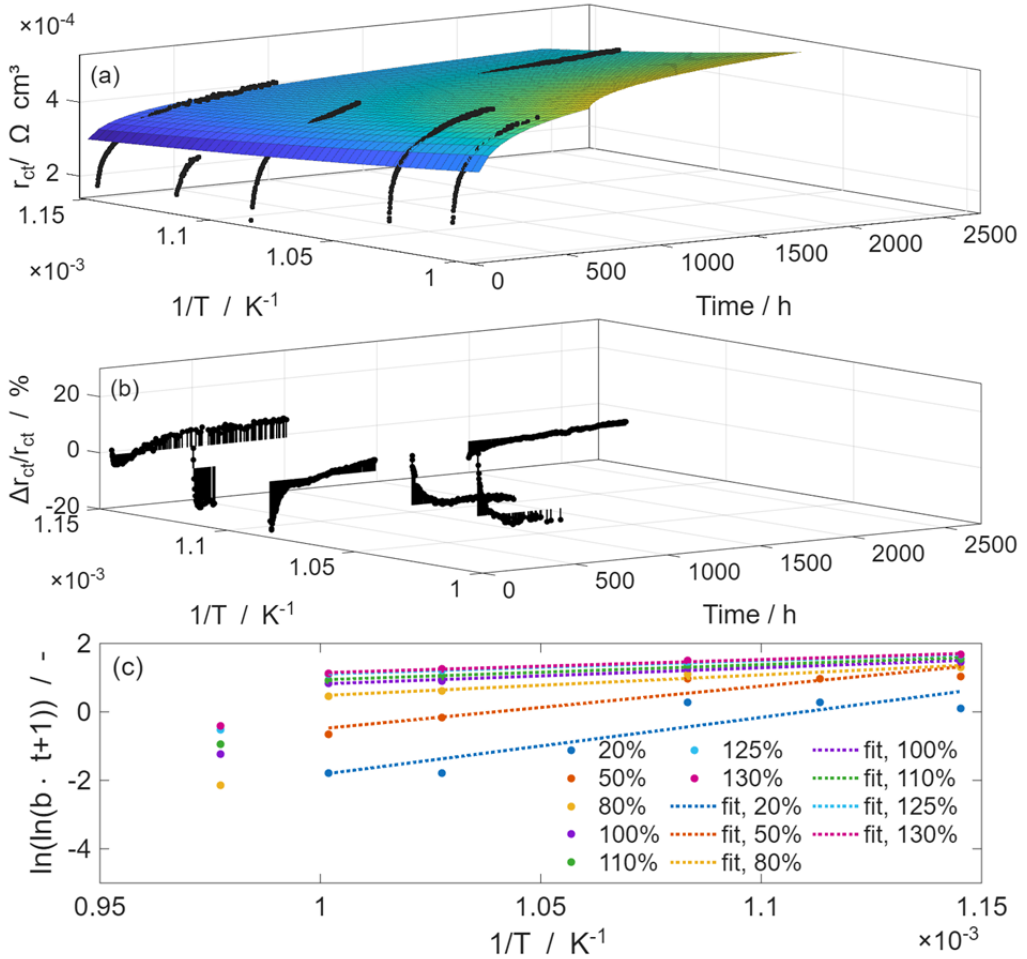


Figure 4.52: (a) The fit results based on Equation 4.28 from the standardized r_{ct} at 600-725 °C and (b) The fit residues. (c) $\ln(\ln(b \cdot t + 1))$ against $1/T$ for cells 1-6 with $b = 0.2251$. Adapted from (7).

To verify the double-logarithm $\ln(\ln(b \cdot t + 1))$ following Arrhenius behavior, this term is plotted against $1/T$ for cells 1–6, as shown in Figure 4.52(c). The t values are from Table 4.15.

A good linear correlation is observed, except at 750 °C. After removing, the linear fitting results are listed in Table 4.19. The quality of the fit improved consistently as degradation levels increased, similar to the Arrhenius power-law model. At lower degradation levels, the fit quality was poor, partly because of competing degradation mechanisms. $E_{a,age}$ decreases and stabilizes around

32.1 kJ/mol, approximately 16.6% smaller than the value derived from the direct fit, cause the latter puts more weight on the early-stage aging, leading to larger values.

Table 4.19: Fitted parameter $E_{a,age}$ for Equation 4.28.

Parameter	$(r_{\text{ct}} - r_{\text{ct,ref}})/r_{\text{ct,ref}} / \%$						
	20	50	110	80	100	125	130
$E_{\text{a,age}} / \text{kJ/mol}$	103.7	138.9	50.4	39.4	37.0	32.8	32.1
R_{fit}	0.798	0.876	0.955	0.966	0.979	0.994	0.990

The expression of the prediction for r_{ct} at 600 °C is:

$$r_{ct}(t, 600 \text{ °C}) = 1.80 \cdot 10^{-4} + 3.83 \cdot 10^{-5} \ln(0.2251 \cdot t + 1) \Omega\text{cm}^3,$$

The predicted r_{ct} values for 10,000 h and 100,000 h are $4.75 \cdot 10^{-4}$ and $5.64 \cdot 10^{-4} \Omega\text{cm}^3$, respectively.

4.5.3.9 Equivalent Time Concept Based on Arrhenius-Based Degradation Behavior and Logarithm Growth

With the previously derived activation energy, the equivalent time at 600 °C required to reach the same degradation level as that at elevated temperature can be calculated using the following transformation with $b = 0.2251$:

$$\ln(b \cdot t_{600^\circ\text{C}} + 1) = \ln(b \cdot t_{\text{elevated}} + 1) \cdot \exp\left(\frac{E_{a,age}}{R_g} \left(\frac{1}{873.15 \text{ K}} - \frac{1}{T_{\text{elevated}}}\right)\right) \Rightarrow \quad (4.30)$$

$$t_{600^\circ\text{C}} = \frac{1}{b} \exp\left[\ln(b \cdot t_{\text{elevated}} + 1) \cdot \exp\left(\frac{E_{a,age}}{R_g} \left(\frac{1}{873.15 \text{ K}} - \frac{1}{T_{\text{elevated}}}\right)\right)\right] - \frac{1}{b} \quad (4.31)$$

Following this, the datasets for cells 1–5 were horizontally stretched and compared to the original 600 °C dataset using $E_{a,age}=38.5 \text{ kJ/mol}$, as shown in Figure 4.53(a).

Within the zoomed-in window, the stretched data at 625 °C fall outside the $\pm 10\%$ error bounds. The stretched data at 650 °C closely follow the error bounds, except during the first 10 h. Data

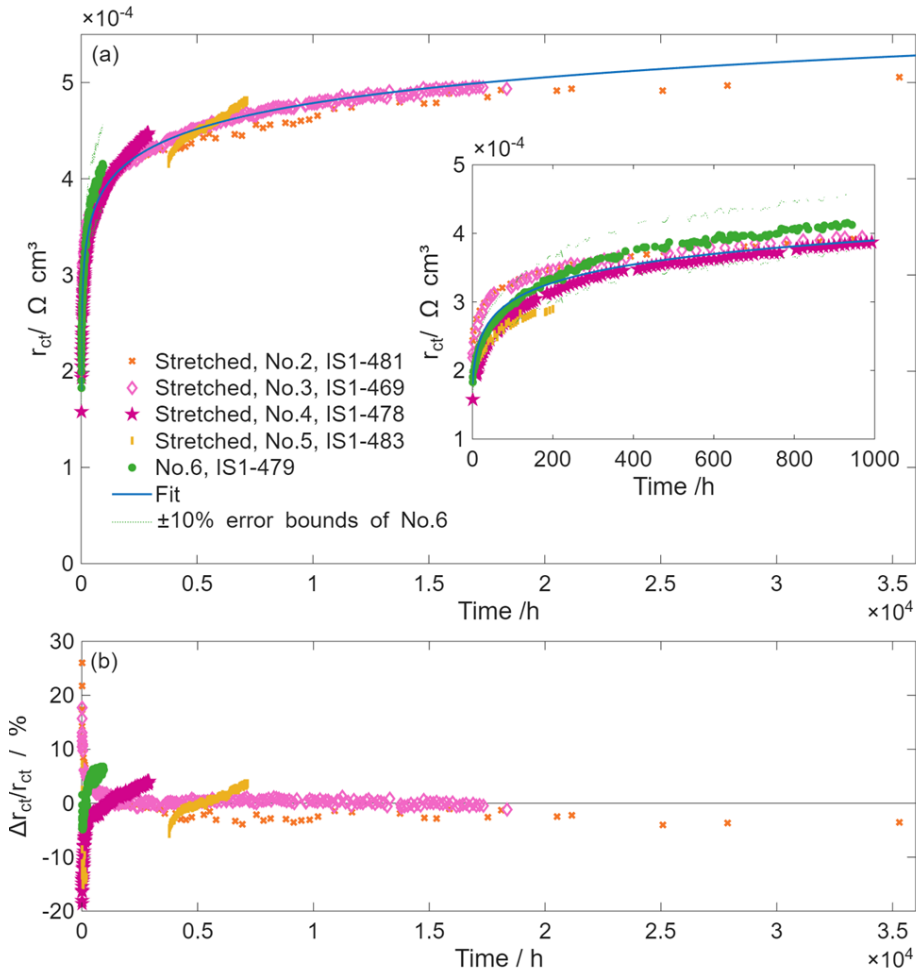


Figure 4.53: (a) The horizontally stretched r_{ct} -time datasets are compared to the data from 600 °C and the fit result based on Equation 4.28. (b) The fit residues. Adapted from (7).

stretched from higher temperatures slightly overestimate aging before 400 h, but underestimate thereafter.

This enables prediction of r_{ct} up to 35,286 h at 600 °C from data at 725 °C. Compared to the model in section 4.5.3.7, the stretching factor is not constant but increases with t , reflecting the logarithmic nature of a potential saturation in the degradation. To predict r_{ct} at 100,000 h, the required test duration at 725 °C would be 780 h. Due to the limited time of this work, the related result is not feasible. Therefore, long-term prediction still relies on fitting Equation 4.28. The logarithm aging model for 600 °C is expressed as:

$$r_{\text{ct}}(t, 600\text{ }^{\circ}\text{C}) = 1.80 \cdot 10^{-4} + a \cdot \exp\left(\frac{-38.5\text{ kJ/mol}}{R_{\text{g}} \cdot 873.15\text{ K}}\right) \cdot \ln(0.2251 \cdot t + 1) \Omega\text{cm}^3.$$

The fit was performed on the four stretched datasets at 625–725 °C and the original data at 600 °C. The fitted parameters are $a = 7.8 \cdot 10^{-3}$ with $R_{\text{fit}} = 0.999$. The fit results and corresponding residuals are plotted in Figure 4.53.

The residuals show a similar trend as in Figure 4.51(b), with large values within the first 200 h due to initial overestimation. Afterwards, the fit falls within $\pm 10\%$ error bounds, with a tendency to underestimate. The long-term predictions from the logarithm fit yield $r_{\text{ct}} = 4.79 \cdot 10^{-4} \Omega\text{cm}^3$ at 10,000 h and $r_{\text{ct}} = 5.68 \cdot 10^{-4} \Omega\text{cm}^3$ at 100,000 h. Overall, the logarithm model provides more conservative long-term predictions due to its naturally slowing growth.

4.5.4 Summary

This section systematically investigates the aging behavior of Ni/GDC electrodes of V1.5a under various operating conditions, focusing on charge-transfer resistance (r_{ct}) as a key indicator of degradation. The electrode of this cell type exhibits excellent initial performance even without a GDC interlayer due to the lower sintering temperature, and a mild reduction protocol yields a fine microstructure while maintaining high mechanical stability and reproducibility. The deviations of fitted r_{ct} is within $\pm 7.4\%$.

Comparisons of cells operated under different conditions have traditionally relied on measurements taken under a nominal condition before and after durability testing (21). In this work, this limited, pointwise comparison strategy is transformed into a systematic, continuous data standardization methodology. By mapping polarization resistance data acquired at different temperatures and humidities to a unified reference condition (600 °C, 50% humidity in hydrogen), this approach enables direct inter-cell comparability. It provides a physically consistent basis for aging and lifetime modeling.

Experimental results demonstrate a clear thermally activated degradation mechanism consistent with Arrhenius kinetics, where elevated temperatures accelerate the increase in r_{ct} . Humidity also significantly influences aging, with higher steam content leading to faster degradation. At the highest tested temperature (750 °C), deviations suggest the activation of different or additional degradation mechanisms.

Multiple modeling approaches were applied to predict the long-term evolution of r_{ct} at 600 °C, as listed in Table 4.20. Predictions are made for 10,000 and 100,000 hours, summarized in Table 4.21 and Figure 4.54.

Table 4.20: The degradation models applied for r_{ct} at 600 °C

No	Model	Expression / Ωcm^3
1	Arrhenius degradation	$r_{ct}(600^\circ\text{C}, t) = 3.87 \cdot 10^{-4} + 6.42 \cdot 10^{-8} \cdot (t - 450)$
2	Power function	$r_{ct}(600^\circ\text{C}, t) = 1.80 \cdot 10^{-4} + 2.60 \cdot 10^{-5} \cdot t^{0.326}$
3	Logarithm growth	$r_{ct}(600^\circ\text{C}, t) = 1.80 \cdot 10^{-4} + 5.34 \cdot 10^{-5} \cdot \ln(0.085 \cdot t + 1)$
4	Polynomial for equivalent time concept	$r_{ct}(750^\circ\text{C}, t_{750^\circ\text{C}})$ stretched following: $4.382t_{750^\circ\text{C}}^2 + 202.3t_{750^\circ\text{C}} + 39.8$
5	Power for equivalent time concept	$r_{ct}(750^\circ\text{C}, t_{750^\circ\text{C}})$ stretched following: $t_{600^\circ\text{C}} = 239.2 \cdot t_{750^\circ\text{C}}^{0.961}$
6	Arrhenius degradation with power function	$r_{ct}(600^\circ\text{C}, t) = 1.80 \cdot 10^{-4} + 3.37 \cdot 10^{-5} \cdot t^{0.2437}$
7	Equivalent time concept based on Arrhenius degradation behavior and power law	$r_{ct}(600^\circ\text{C}, t) = 1.80 \cdot 10^{-4} + 4.012 \cdot 10^{-5} \cdot t^{0.2440}$
8	Arrhenius degradation with logarithmic growth	$r_{ct}(600^\circ\text{C}, t) = 1.80 \cdot 10^{-4} + 3.83 \cdot 10^{-5} \cdot \ln(0.2251 \cdot t + 1)$
9	Equivalent time concept based on Arrhenius degradation behavior and logarithmic growth	$r_{ct}(600^\circ\text{C}, t) = 1.80 \cdot 10^{-4} + 3.88 \cdot 10^{-5} \cdot \ln(0.2251 \cdot t + 1)$

As presented in Figure 4.54(a), all models (except Model 6) applied in this work reproduce the degradation evolution accurately after approximately 100 h. Their tendencies start to diverge before 1000 h. Using the data at 600 °C (cell No. 6, IS1-479) as a reference, Models 1 and 2 show a slight tendency to overestimate, whereas Models 4 and 5 appear to agree well with the measured data. The other models exhibit a slight tendency to underestimate, especially Model 6.

At larger timescales, differences between the models become evident. The predictions of Models 1 and 2 exhibit a pronounced tendency to overestimation. As shown in Figure 4.54(b), the standardized r_{ct} values of cell No. 5 (IS1-483, operated at 625 °C) remain significantly below their values, which contradicts the expected thermally activated aging. Consequently, Models 1 and 2 are regarded as physically implausible and are excluded from further consideration.

In contrast, logarithmic-based models combining the Arrhenius degradation (Models 8 and 9) predict a lower degradation rate or a stronger deceleration of aging, potentially leading to an underestimation of long-term degradation.

Notably, the evolution of Models 3–9 is highly consistent over the first 10,000 h, both qualitatively and quantitatively. As summarized in Table 4.21, the predicted r_{ct} values at 10,000 h yield

Table 4.21: Predicted r_{ct} and R_{Pol} values at 10,000 h and 100,000 h.

Model	10,000 h		100,000 h	
No.	r_{ct} ($\Omega \text{ cm}^3$)	R_{Pol} ($\Omega \text{ cm}^2$)	r_{ct} ($\Omega \text{ cm}^3$)	R_{Pol} ($\Omega \text{ cm}^2$)
1	$1.00 \cdot 10^{-3}$	1.31	$6.78 \cdot 10^{-3}$	8.50
2	$7.10 \cdot 10^{-4}$	0.94	$1.29 \cdot 10^{-3}$	1.67
3	$5.41 \cdot 10^{-4}$	0.74	$6.63 \cdot 10^{-4}$	0.91
4	$5.43 \cdot 10^{-4}$	0.74	$6.42 \cdot 10^{-4}$	0.86
5	$5.72 \cdot 10^{-4}$	0.77	$> 7.29 \cdot 10^{-4}$	> 0.97
6	$5.61 \cdot 10^{-4}$	0.68	$8.47 \cdot 10^{-4}$	0.98
7	$5.65 \cdot 10^{-4}$	0.76	$8.45 \cdot 10^{-4}$	1.12
8	$4.75 \cdot 10^{-4}$	0.63	$5.64 \cdot 10^{-4}$	0.76
9	$4.79 \cdot 10^{-4}$	0.64	$5.64 \cdot 10^{-4}$	0.76

an average of $5.34 \cdot 10^{-4} \Omega \text{ cm}^3$ with a relative dispersion (STD/AVG) of $\pm 7.56\%$. This convergence indicates that, despite the absence of explicit physical constraints in some models, the predictions are mutually consistent and credible. The prediction discrepancies increase over time. At 100,000 h, the average predicted r_{ct} is $6.88 \cdot 10^{-4} \Omega \text{ cm}^3$, with a relative deviation of $\pm 18.7\%$. This level of error is acceptable for an initial industrial assessment during product development.

However, this also highlights the limitations of the modeling approach used in this work. To validate the developed models, operation times beyond 10,000 h would be necessary, as all models remain within a narrow range in the available timescale. Therefore, it is not possible to conclusively determine which model fits best within this study.

Using the parameters listed in Tables 4.8 and 4.9, together with the fitted chemical capacitance $C_{chem} = 45.7 \text{ C cm}^{-3}$ obtained from the pristine cell No. 7 (IS1-474_V1.5a), the predicted r_{ct} values are converted into polarization resistance contributions associated with the LF_2 and MF_1 processes. This conversion is performed based on Equations 2.68, 2.69, and 2.70. The measured data of cell No. 6 (IS1-479_V1.5a) and the predictions from Models 1–9 are compared in Figure 4.55. The corresponding values at 10,000 and 100,000 h are summarized in Table 4.21.

The predicted polarization resistance $R_{Pol,EL}$ exhibits the same qualitative trends as r_{ct} . Consistent with the charge-transfer resistance analysis, Models 1 and 2 are excluded due to clear overestimation. For the remaining models, the prediction uncertainty of $R_{Pol,EL}$ is comparable to that observed for r_{ct} . At 10,000 h, the predicted $R_{Pol,EL}$ values yield an average of $0.708 \Omega \text{ cm}^2$ with a relative deviation of $\pm 8.12\%$, representing a narrow prediction band and indicating good

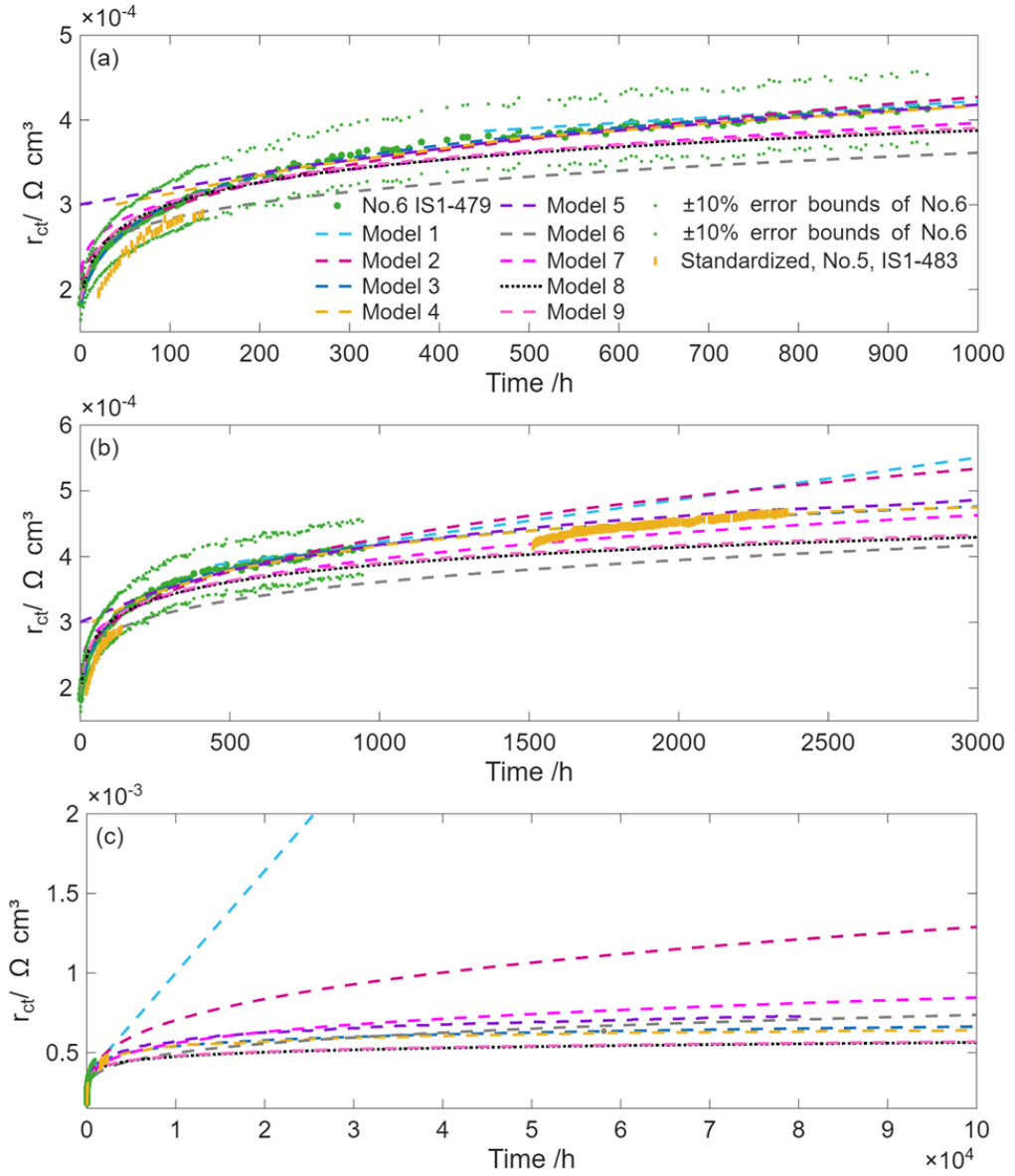


Figure 4.54: (a) The modeling results based on models 1-9 compared to the real measurement at 625 °C and nominal conditions. The thin dashed lines indicate a $\pm 10\%$ error bound of the measured data at 600 °C. (b) A comparison of the prediction of models 1-9 up to 3,000 h. (c) A comparison of the prediction of models 1-9 up to 100,000 h. Adapted from (7).

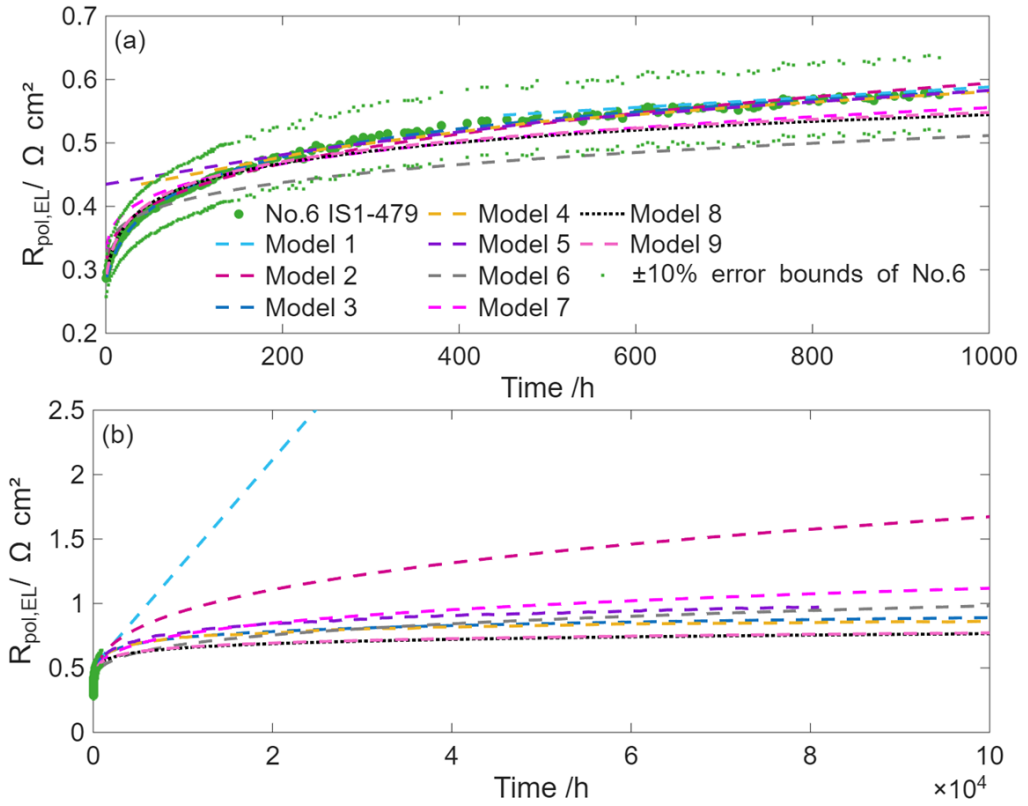


Figure 4.55: (a) The modeling results of polarization resistance based on models 1-9 compared to the real measurement at nominal conditions. The thin dashed lines indicate a $\pm 10\%$ error bound of the measured data at 600 °C. (b) A comparison of the prediction of models 1-9 up to 100,000 h. Adapted from (7).

predictive consistency. At 100,000 h, the average increases to $0.899 \Omega \text{ cm}^2$ with a relative deviation of $\pm 15.3\%$. With this aging modeling method extended to the cell or even the stack level, the power degradation rate at a constant-current operating point can be derived from Equation 2.38.

Overall, the real long-term degradation behavior is expected to lie between the bounds defined by the power-law and logarithmic growth models, with the combination of Arrhenius behavior fits providing physically meaningful and reliable extrapolations. This comprehensive comparison implies the importance of selecting models that balance empirical fit quality with physical plausibility when projecting SOFC electrode aging over industrially relevant timescales.

5 Summary

In the market development for solid oxide fuel cells, excellent performance and reliable operation for up to 100,000 h are two essential requirements. Compared to the widely studied Ni/YSZ anode, the introduction of GDC has attracted increasing attention due to its mixed ionic and electronic conductivity. This material exhibits higher conductivity at low to intermediate temperatures (below 600 °C) and enables electrochemical reactions to occur not only at the TPB but also at the DPB. As a result, the Ni/GDC electrode tends to exhibit greater resistance to degradation and sulfur poisoning.

The objective of this work is to follow the full development pathway of the Ni/GDC electrode for operation at 600 °C. To eliminate the influence of the cathode, electrolyte-supported symmetrical Ni/GDC cells were selected. The work is divided into five parts: (i) development of a novel multi-cell testing method to reduce time and cost, (ii) optimization of performance using different fabrication techniques, (iii) sensitivity tests to identify loss processes in the electrode and to establish an equivalent circuit model for CNLS-fitting, (iv) investigation of both electrochemical and structural degradation behavior under accelerated stress conditions to design an appropriate aging test protocol, and (v) introduction of a novel data processing method enabling direct comparison between cells operated under different conditions, followed by semi-empirical aging modeling.

After completing these five steps, a high-performance Ni/GDC electrode operating at 600 °C was developed. The chosen degradation indicator is the charge transfer resistance, which can be predicted to be $6.88 \cdot 10^{-4} \Omega \text{cm}^2$ with an error below 20 % at 100,000 h. The predicted polarization resistance is $0.899 \Omega \text{cm}^2$, with an error exceeding 15.3 %, but it is still sufficient for early-stage commercial validation of the SOFC electrode.

The following sections summarize the testing methods, results, and main conclusions.

Test Method Validation To reduce the cost of aging tests, a new concept employing an active-driven gas layer for symmetrical cells was introduced. Compared with the conventional single-cell test setup, multiple cells were vertically aligned, with only Ni meshes between them, enabling simultaneous EIS measurements. The goals were to achieve, in a single experiment: (i)

several identical cells operated under the same conditions for different durations, and (ii) several different cells operated under identical conditions for direct comparison.

The first approach proved highly effective. A smaller gas-diffusion loss was observed due to the shorter diffusion path between the cells. However, an extraordinary pseudo-inductive loop appeared in the impedance spectra during tests with different cells. After reviewing all measurement data, it was determined that this phenomenon occurred only in cells adjacent to lower-performing cells.

A simplified physical model was established to explain this effect. When identical cells are tested together, the gas produced near one electrode equals the gas consumed near the adjacent electrode, resulting in a symmetric gas atmosphere across each cell. This balance is disrupted when neighboring cells perform worse, leading to an asymmetric atmosphere across the cell and a non-zero Nernst voltage, which appears as an inductive loop in the impedance spectrum.

A mathematical simulation based on this physical model was performed in MATLAB and successfully reproduced the experimental observations. The simulation also indicated a potential overestimation of the measured impedance when two high-performing cells are adjacent. Consequently, only identical cells should be tested together in this setup.

Initial Characterization In this work, a target polarization resistance of $0.25 \Omega\text{cm}^2$ at 600°C and 50% humidity was adopted based on the low-frequency arc of the full-cell performance reported by Ceres Power under similar conditions (276).

To improve performance, several fabrication techniques were evaluated: (i) screen printing using usual Jülich paste (V1, V2), (ii) screen printing using fine particle paste (V3, V5), (iii) infiltration of Ni into a GDC skeleton (V4), and (iv) infiltration of GDC into a Ni skeleton (V6).

Additionally, several fabrication factors were investigated: (i) sintering temperature, (ii) a GDC interlayer, (iii) solution concentration, and (iv) particle size of the current collector layer.

Initial electrochemical and structural analyses indicated that the electrode of V4 performed best, with fine Ni particles effectively activating the GDC surface. The next best were V3 and V6, featuring very fine GDC structures and a large DPB. The weakest performance was observed in variants V1, 2 and 5, which had a coarse microstructure due to large particle size and high sintering temperature. Among all fabrication parameters, sintering temperature was found to be the most critical. Most variants performed better at lower sintering temperatures due to finer electrode microstructures, except for V3.12c, likely due to insufficient percolation of the GDC phase. The GDC interlayer slightly improved performance, likely by enhancing adhesion between the electrolyte and electrode.

The applied infiltration concentration appeared high, reaching saturation after the first infiltration. Additional infiltration showed almost no improvement, and in some cases even deterioration, due to particle agglomeration. Generally, a smaller particle size in the current collector layer resulted in lower polarization resistance. SEM analysis revealed incomplete coverage of the contact layer on the electrode when larger particles were used, resulting in a reduced active area.

After initial characterization, only variants demonstrating both high electrochemical performance and/or mechanical stability were selected for further analysis. These were V1, V3.12, V4.4, V4.5 and V6.

Sensitivity Test In common SOFC aging studies, voltage decay over time is typically monitored. However, this is not feasible for symmetrical cells. Instead, the area-specific resistance serves as a more suitable degradation indicator, from which voltage degradation can be inferred. Since this study focuses on anode modeling, it is crucial to identify and isolate its loss processes.

The sensitivity tests involved variation of four parameters: (i) temperature, (ii) steam partial pressure, (iii) hydrogen partial pressure and (iv) inert gas species.

To ensure stable electrode conditions, all tests were conducted only after a steady polarization resistance value was reached at elevated temperatures.

From the characterization of variants V1 and V6, five processes were identified, LF₁, LF₂, MF₁, MF₂ and HF, corresponding to increasing characteristic frequencies. These processes were assigned to gas diffusion, surface reactions, bulk electrode processes, an additional mid-frequency process of unknown origin, and electrolyte/interface processes, respectively.

Consequently, an equivalent circuit model was established, consisting of one ohmic resistance, one transmission line model (TLM) element, and three RQ elements. The RQ element representing gas diffusion was assigned a fixed value before fitting. The geometry factor was calculated using Equation 4.18, based on resistance changes when alternating the inert gas. The diffusion resistance was then calculated under the given temperature and atmospheric conditions. The TLM element represents the electrode processes LF₂+MF₁. The parameter to be fitted, the charge transfer resistance r_{ct} , serves as the key degradation indicator, as it is directly influenced by the TPB and DPB densities. The required structural parameters for initialization were obtained from 3D reconstruction, primarily performed by Dr. Ardavan Makvandi (LEM, KIT) and Dr. Matthias Wieler (Bosch, Renningen). The two remaining RQ elements represent MF₂ and HF, with no restrictions except their respective frequency ranges.

The losses in the electrodes V4.4a and V3.12b were dominated by high-frequency processes, which overshadowed electrode-related features and made CNLS fitting unreliable. Cell V4.5a

exhibited impedance similar to that of V1 and V6, but its fine Ni structure prevented testing at elevated temperatures. At 600 °C, this variant showed continuous degradation over 1000 h, with no stabilization observed within the allowed time frame. Therefore, V4.5a was excluded from further analysis.

Test at Elevated Temperatures The design of the accelerated stress test protocol is crucial, as the dominant aging mechanisms may differ under varying conditions. The tests in this work were designed to accelerate the specific degradation mechanisms occurring at 600 °C and 50 % steam. Cells from V1 and V6 were operated at elevated temperatures up to 900 °C and under varying humidity levels (10–50%). The main findings were analyzed using both electrochemical and structural characterization. For screen-printed variant V1:

- 900°C, 50% humidity: Cells from V1.2 showed continuous improvement in polarization resistance up to 1,100 h. However, both SEM images and 3D reconstructions revealed clear structural degradation, including decreased TPB and DPB densities. This discrepancy may be attributed to surface diffusion of Ni into the GDC interlayer, indicating that this layer also participates in the electrochemical reaction and restricts performance. To exclude its influence, cell IS1-470_V1.5a, without an interlayer, was tested under the same conditions. Only degradation was observed, suggesting that the apparent improvement might be related to the interlayer.
- 800 °C, 50% humidity: Under this condition, the screen-printed reference cell IS1-443_Ref1 initially showed degradation, followed by a slight improvement, and then stabilization. However, a sudden increase in both polarization and ohmic resistance occurred before a second plateau was reached. This phenomenon could be induced by the chemical expansion of the GDC phase, which becomes more pronounced at high temperature. Such deterioration was not observed in Ni/GDC cells, which exhibited gradual but decelerating degradation. This difference may result from the higher volume fraction of the Ni phase, which likely dilutes internal stresses. Nevertheless, this chemical expansion should be avoided, as it introduces an additional degradation mechanism unlikely to be present under nominal operating conditions.
- 800 °C, 10% humidity: Compared with cell IS1-443_V1.2 operated at higher humidity (50%), this cell IS1-445_V1.2 exhibited a clear performance improvement. This can be attributed to relatively stronger surface diffusion of Ni, as gas-phase diffusion of Ni species weakens at lower humidity.
- ≤ 750 °C, 50% humidity: Under these conditions, the degradation was mainly located in the low-frequency region of the impedance spectra. This is consistent with the observed

structural changes, such as Ni coarsening and a decrease in TPB/DPB densities. The GDC phase remained stable, as both its particle size and tortuosity showed minimal variation.

Infiltrated variant V6 showed similar temperature-dependent aging behavior as the V1 variants, except during the initial short-term period. This difference may be related to its superior initial performance and corresponding sharp degradation during the first 30–100 h. At 900 °C, strong sintering effects were observed in the GDC phase due to its high mobility, leading to potential electrode reorganization and complicating the interpretation of the aging mechanism. Moreover, since the GDC interlayer is inevitable in this cell type, it was excluded from aging modeling.

In conclusion, variant V1.5a (without interlayer), which showed excellent initial performance, clearly isolated low- and mid-frequency processes, and enabled accessible structural analysis, was selected for aging analysis and modeling. For the test protocol, the maximum temperature was set to 750 °C to suppress chemical expansion effects and prevent electrode reorganization. The goal was to preserve the GDC structure and ensure that the dominant aging mechanism of the nominal operating condition remained representative.

Another objective of this work was to establish a physically based model that correlates the charge transfer resistance r_{ct} with the TPB and DPB densities. Compared to existing models (22, 193), the inclusion of DPB exponentially increases the modeling complexity. Instead of a simple function linking the Ni particle radius to TPB density, a relationship incorporating TPB, DPB, and DPB activation should be developed. Quantifying the last term is challenging because small Ni particles in variant V4 cannot be resolved with FIB/SEM. Even when resolvable Ni particles are present, it remains unclear whether the TPB, the activation of the GDC surface, or both are responsible for the observed performance.

The qualitative analysis of the relationship between structural parameters and charge transfer resistance presented in this work provides valuable insights into the impact of TPB and DPB on performance. However, it is insufficient to describe the coupling. A systematic study involving cells with gradually increasing Ni particle sizes would be performed to identify the threshold for reaction onset at TPBs. To accurately capture the degradation trends, a physically based model describing the interdependence is essential. This comprehensive study is beyond the frame of the present work. As a compromise, the subsequent aging modeling was based on fitted r_{ct} values using semi-empirical functions.

Aging Behavior Analysis and Modeling In existing studies on cell-level aging models based on accelerated stress tests, comparisons among cells are typically limited to one or two data points. In this work, a novel test protocol and subsequent data-processing method enable, for the first time, a continuous and direct comparison among cells operated at different temperatures and

humidity levels along the time axis. The standardization substantially increases the size of the available dataset, thereby improving both the selection of mathematical functions and the quality of model fitting.

Cells from V1.5a were operated at temperatures ranging from 600 °C to 750 °C and humidities between 10–50%. Every several hundred hours, the cell was cooled to 600 °C or the atmosphere was adjusted to 50% humidity in hydrogen for a reference measurement. The fitted r_{ct} from these reference measurements over time clearly indicates thermal and humidity-activated degradation.

According to previous studies, r_{ct} follows Arrhenius behavior with respect to temperature and a power-law dependence on the steam partial pressure. This implies the existence of a constant factor following the Arrhenius equation, which relates r_{ct} values between two temperatures. A similar constant exists for varying humidities. The r_{ct} – t data series obtained at higher temperatures or lower humidity were standardized by multiplying the raw data by the corresponding conversion factor F_c .

The models applied in this work include: (1) Arrhenius degradation (linear increase), (2) Power function, (3) Logarithmic decay, (4) Polynomial function (degree=2) for the equivalent time concept, (5) Power function for the equivalent time concept, (6) Arrhenius degradation with power function, (7) Equivalent time concept based on Arrhenius degradation and power law, (8) Arrhenius degradation with logarithmic decay, and (9) Equivalent time concept based on Arrhenius degradation and logarithmic decay.

All models can be applied for varying temperatures, while only Models 2–5 can be applied for varying humidity. We found an additional dominant aging mechanism at 750 °C using Arrhenius-based models, which is therefore excluded from this modeling approach.

Under nominal conditions, all models agree well with the experimental data after approximately 100 h. The initial deviations are likely due to electrode stabilization and competing aging mechanisms. Over longer time scales, the prediction results begin to diverge. Models 1 and 2 tend to overestimate degradation. At 10,000 h, the predicted r_{ct} values of the other 7 models fall within $\pm 7.56\%$ of $5.34 \times 10^{-4} \Omega \text{ cm}^3$. Such small deviations make experimental validation within 10,000 h practically impossible. At 100,000 h, the predicted r_{ct} values have an average of $6.88 \times 10^{-4} \Omega \text{ cm}^3$ with a deviation of $\pm 18.7\%$, which decreases to $\pm 15.3\%$ when considering the corresponding polarization resistance.

Models that combine Arrhenius behavior with mathematical functions demonstrate superior fit quality and robustness due to reduced dependence on initial parameterization. Further combination with the equivalent time concept induces only minor variations, which can be neglected in the context of this work.

Conclusion In this work, a complete workflow for SOFC electrode development was established and demonstrated. A novel multi-cell test method was developed, enabling a significant reduction of experimental cost while maintaining high data quality. Through detailed electrochemical analysis, the relevant loss processes were identified, enabling the construction of a physically meaningful equivalent circuit based on a transmission-line model.

Accelerated stress tests were conducted below 750 °C, and a reference-measurement-based standardization procedure was introduced to convert datasets obtained at various temperatures and humidities to nominal conditions. This standardization greatly increased the effective data volume for model development, leading to improved robustness and reliability of model fitting. Semi-empirical functions, combined with physically constrained terms such as Arrhenius degradation, further enhanced model stability by minimizing sensitivity to initialization.

The adaptation of the equivalent degradation concept, in our case the equivalent time concept, provides an efficient tool for gaining a first impression of long-term degradation trends. Within the workflow developed here, nine aging models were evaluated. Except for two models that failed to capture the aging trends, the remaining seven provided highly consistent and accurate predictions within a narrow range, sufficient for early-stage industrial development.

Overall, the presented workflow, or part of it, can be applied broadly across electrochemical systems at different levels. In particular, the use of reference measurements for the standardization of accelerated stress testing can be generalized to other degradation indicators. The methodology established in this work thus offers a fast and cost-effective approach for assessing the long-term behavior of complex electrochemical systems.

A Appendix

A.1 Simulink Model for Ni/GDC Anode

Modeling in Simulink

The simulation based on the transmission line model was performed in Simulink. To simplify impedance generation and calculation, the *Simscape Electrical Specialized Power Systems* block-set was employed, using a conventional capacitance in place of a constant phase element (CPE). As shown in Figure A.1(a), the fundamental element represents a 0.1 μm -thick electrode segment with an active area of $1 \cdot 1 \text{ cm}^2$.

The upper rail represents the ionic rail. R_{ion} (in Ω) denotes the ionic resistance, while R_{eon} (in Ω) represents the electronic resistance. The *Charge_Transfer* block includes the charge transfer resistance R_{ct} (in Ω) and the chemical capacitance C_{ct} (in F). All parameters are defined in the model workspace and can be manually adjusted.

Repeating the fundamental element ten times yields an equivalent layer thickness of 1 μm (Figure A.1(d)). Based on the SEM results, the anode of cell IS1-474_V1.5a has a thickness of 8 μm , corresponding to eight series repetitions of this element, as shown in Figure A.1(e). Other cells exhibit similar electrode thicknesses and can be modified by adding or removing 1 μm elements.

The *powergui* block shown in Figure A.1(e) and Figure A.2(a) serves as the central control unit for the simulation environment. In this work, the simulation type is set to *Continuous*, and the analysis tool (App) selected is the *Impedance Calculator*. The *Impedance Measurement* block is employed to compute the frequency-dependent impedance of an arbitrary electrical network.

During the simulation, the user interface illustrated in Figure A.2(c) appears, allowing the user to adjust the frequency range. In this study, the same measurement points as in the real electrochemical experiment were used. The resulting impedance spectra were exported to the MATLAB workspace and subsequently analyzed using the DRT method.

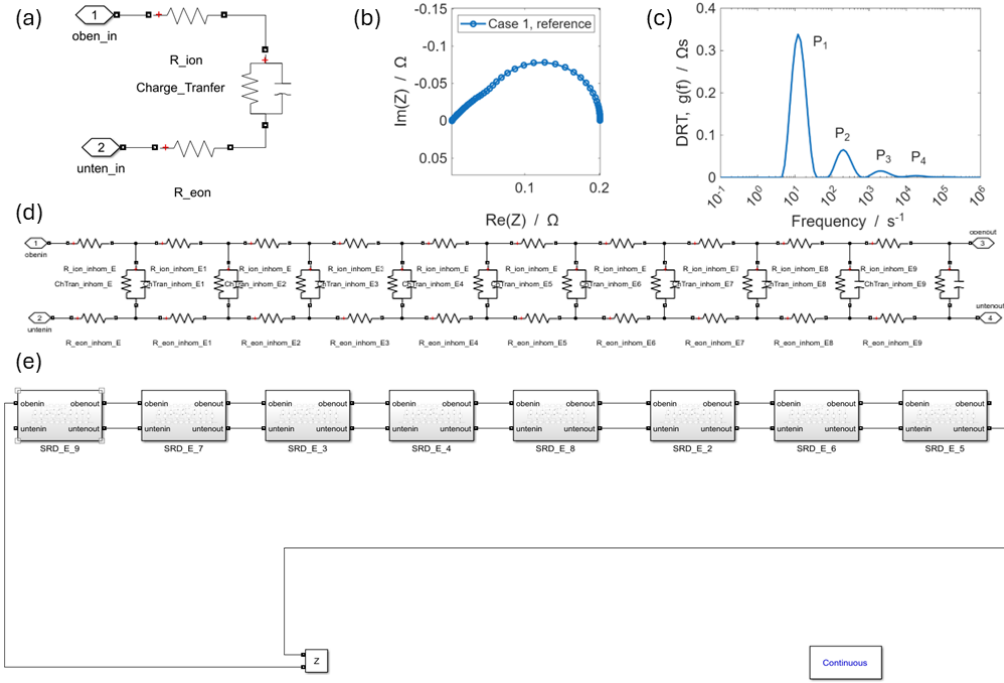


Figure A.1: (a) Fundamental element for TLM, equaling a $0.1 \mu\text{m}$ thick layer. (b) An exemplary impedance generated based on the (e) full Simulink model with parameters of Case 1 as listed in Table A.1 and (c) corresponding DRT. (d) A $1 \mu\text{m}$ thick layer from 10 repetitions of the fundamental element. (e) A full Simulink model representing an $8 \mu\text{m}$ thick electrode with an Impedance Measurement block and powergui block.

A.1.1 Parameter Initialization

Because the simulations in this study are intended for qualitative analysis, the material and structural parameters are taken from (239) for simplicity. The ionic resistance in Figure A.1(a), calculated for a $1 \mu\text{m} \cdot 1 \text{ cm}^2$ volume with GDC volume fraction of 40 % and a tortuosity of 2, is $R_{ion} = 2 \cdot 10^{-3} \Omega$. The electronic resistance is assumed to be extremely small, $R_{ele} = 1 \cdot 10^{-10} \Omega$, due to the high electronic conductivity of Ni under ideal percolation.

Following the same procedure, the charge transfer resistance in the fundamental element is calculated to be $r_{ct} = 12 \Omega$, and the corresponding interfacial capacitance as $C_{ct} = 1.12 \cdot 10^{-3} \text{ F}$.

The parameters for Case 1, used as the reference, are listed in Table A.1. The TLM simulation and the corresponding DRT are shown in Figure A.1(b, c). The polarization resistance is $R_{pol} = 0.199 \Omega$, and the ohmic resistance is $R_{ohm} = 2.07 \cdot 10^{-3} \Omega$. The impedance spectrum exhibits two arcs, with the low-frequency arc dominating the overall polarization losses. The corresponding DRT spectrum contains four peaks (P_1 – P_4). Since only charge transfer and ionic

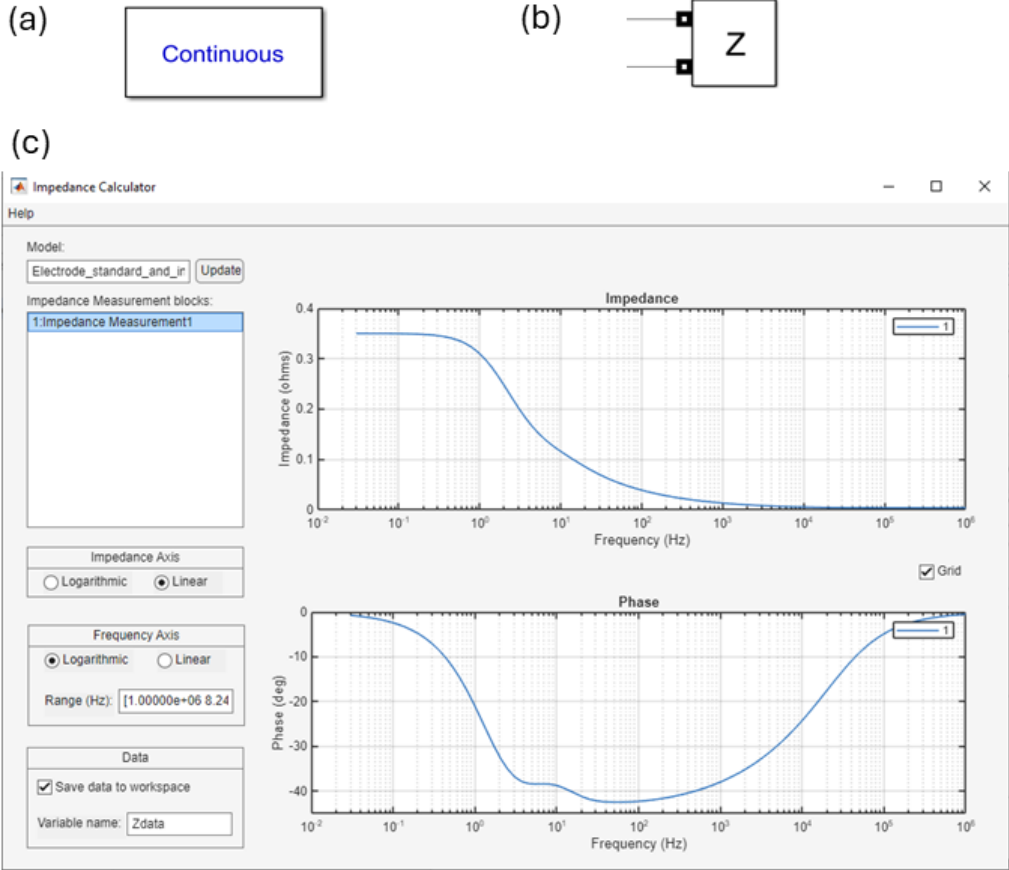


Figure A.2: (a) powergui block, (b) *Impedance Measurement* block and (c) User interface of *Impedance Calculator*.

conduction processes are considered, peaks P_3 and P_4 cannot be assigned to real electrochemical processes. Instead, they might arise from the intrinsic numerical behavior of the TLM during DRT computation, i.e., decaying side peaks.

A.1.2 Influence of Layer Thickness

According to Dierickx (65), the optimal electrode thickness corresponds to the penetration depth calculated using Equation 2.69. In this work, electrode thicknesses of 4 μm (Case 4), 8 μm (Case 1), and 12 μm (Case 5) are compared, as shown in Figure A.3(a, b). The corresponding parameters and the resulting polarization and ohmic resistances are summarized in Table A.1.

Table A.1: Simulation parameters for variation of R_{ion} , R_{eon} , R_{ct} and layer thickness.

Case / Parameter	$R_{\text{ion}} (\Omega)$	$R_{\text{ct}} (\Omega)$	$R_{\text{eon}} (\Omega)$	Layer thickness (μm)	$R_{\text{pol}} (\Omega)$	$R_{\text{ohm}} (\Omega)$
1 (AAAAAAAAA)	$2 \cdot 10^{-3}$	12	$1 \cdot 10^{-10}$	8	0.199	0.00207
2 (BBBBBBBBB)	$2 \cdot 10^{-3}$	6	$1 \cdot 10^{-10}$	8	0.121	0.00207
3 (CCCCCCCCC)	$2 \cdot 10^{-3}$	24	$1 \cdot 10^{-10}$	8	0.352	0.00207
4	$2 \cdot 10^{-3}$	12	$1 \cdot 10^{-10}$	4	0.326	0.00204
5	$2 \cdot 10^{-3}$	12	$1 \cdot 10^{-10}$	12	0.169	0.00212
6	$2 \cdot 10^{-3}$	12	$1 \cdot 10^{-3}$	8	0.175	0.0547
7	$2 \cdot 10^{-3}$	12	$2 \cdot 10^{-3}$	8	0.175	0.0810
8	$4 \cdot 10^{-3}$	12	$1 \cdot 10^{-10}$	8	0.242	0.00399
9	$8 \cdot 10^{-3}$	12	$1 \cdot 10^{-10}$	8	0.316	0.00800

When the layer thickness increases from 4 to 8 μm , the polarization resistance decreases from 0.326 to 0.199 Ω (–39%). With a further increase to 12 μm , the reduction in polarization resistance is only 9.2%, reaching 0.169 Ω . The ohmic resistance increases slightly from 0.00204 to 0.00207 Ω (+1.5%) when the layer thickness doubles. For the increase from 8 to 12 μm , the corresponding rise is 2.4%.

The ideal electrode thickness calculated from Equation 2.69 is 7.75 μm . Therefore, in Case 4, the electrode performance is limited by insufficient electrode thickness. The polarization resistance decreases rapidly with increasing thickness, reaching approximately 7.75 μm (close to Case 1 at 8 μm). As a result, the entire electrode is electrochemically active. Further increases in layer thickness primarily increase the ohmic resistance while contributing little to reaction kinetics. For excessively large thicknesses, the electrode performance becomes limited by gas diffusion (65).

As shown in Figure A.3(b), peak P_1 decreases with increasing layer thickness, and peak P_2 , typically associated with charge transport, increases and shifts toward lower frequencies. When the layer thickness reaches 12 μm , the first two peaks begin to overlap.

A.1.3 Influence of Charge Transfer Resistance

The availability of reaction sites and intrinsic reactivity are critical factors that determine electrode performance. In the simulations, the charge-transfer resistance was varied (Cases 1, 2, and 3) to investigate its effect on the impedance while keeping all other parameters constant. The results are presented in Figure A.3(c, d).

As shown in Table A.1, when the charge-transfer resistance increases from 6 to 12, and finally to 24 Ω , the polarization resistance correspondingly rises from 0.121 to 0.199 and in the end 0.352 Ω . No change is observed in the ohmic resistance. The corresponding ideal electrode thicknesses are 5.5, 7.7, and 11 μm , respectively. This indicates that in Case 3, the electrode performance is limited by both reactivity and electrode thickness.

As illustrated in Figure A.3(d), peak P_1 enlarges with increasing charge transfer resistance and shifts toward lower frequencies. Interestingly, peak P_2 , typically associated with charge transport (ionic conduction), exhibits a similar trend, even though the ionic and electronic resistances are unchanged. This behavior can be attributed to variations in active-layer thickness, in which charge transport and charge transfer are coupled.

A.1.4 Influence of Ionic Resistance

In high-performing infiltrated cells, particularly those with Ni nanoparticles infiltrated in the GDC skeleton, charge transport can be a limiting factor in electrode performance. In the simulations, the ionic resistance increases from $2 \cdot 10^{-3} \Omega$ (Case 1) to $4 \cdot 10^{-3} \Omega$ (Case 8) and finally to $8 \cdot 10^{-3} \Omega$ (Case 9). The results are presented in Figure A.3(e,f).

As listed in Table A.1, significant changes occur in the ohmic resistance. When the ionic resistance doubles, the ohmic resistance nearly doubles as well. A similar trend is observed for the further doubling to $8 \cdot 10^{-3} \Omega$. This behavior is partly due to the thinner active electrode layer, which decreases from 7.7 μm to 5.5 μm and finally to 3.9 μm . In contrast, the increase in polarization resistance is less pronounced, rising from 0.199 to 0.242 Ω (+21.6%) and then to 0.316 Ω (+58.8%). As shown in Figure A.3(f), with deteriorating ionic conduction, the side peaks P_2 – P_4 enlarge and shift toward lower frequencies. In Case 1, P_1 and P_2 are two well-separated peaks, which begin to overlap in Case 8. In Case 9, the overlap is pronounced. P_1 broadens, and the other side peaks are barely visible. This indicates that poor ionic conduction limits electrode performance.

A.1.5 Influence of Electronic Resistance

In typical Ni/YSZ electrodes, electronic conduction occurs only via a percolated Ni phase, so the electronic resistance can generally be neglected due to the high metallic conductivity of Ni. In this work, structural analysis of the Ni/GDC cermet revealed no Ni percolation (i.e., isolated Ni phase) except in cell type V6. Therefore, electronic conduction occurs primarily through the GDC phase, and R_{con} must be considered. The electronic resistance increases from 0 Ω (Case 1)

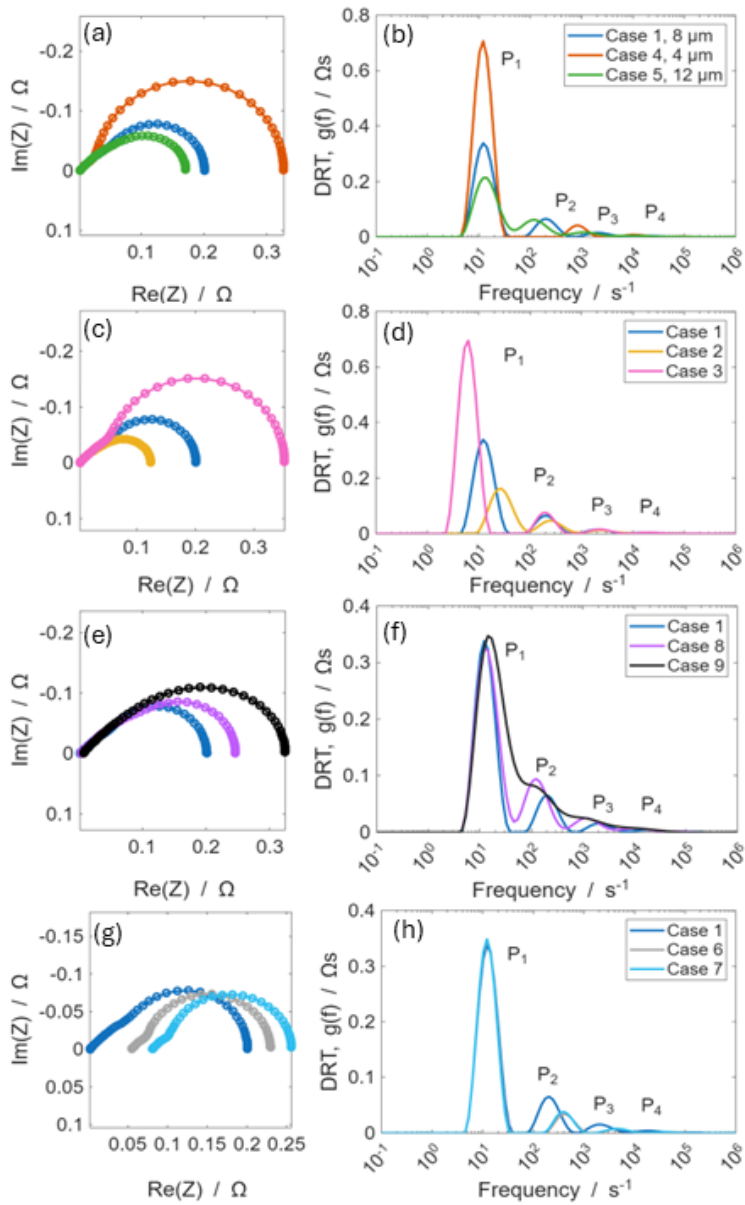


Figure A.3: The simulated impedances and corresponding DRTs regarding the impact of (a, b) layer thickness, (c, d) charge transfer resistance, (e, f) ionic conduction, and (g, h) electronic conduction. Legend corresponds to the first column of Table A.1.

to half of the ionic resistance (Case 6) and finally equals the ionic resistance (Case 7, not possible in reality). The results are shown in Figure A.3(g,h).

The ideal electrode thickness decreases from 7.7 to 6.3, and finally to 5.5 μm . Consequently, the ohmic resistance increases, with Case 7 exhibiting more than a 40-fold increase compared to the reference. Interestingly, the polarization resistance decreases despite worsening electronic conduction. The DRTs in Figure A.3(h) indicate that peak P_1 (charge transfer) remains largely unaffected, while the side peaks P_2 – P_4 decrease in magnitude and shift to higher frequencies.

In this RC-ladder analogy, increasing the electronic resistance redistributes the voltages across the series of charge-transfer elements, thereby reducing the total impedance semicircle over the simulated frequency range. This behavior is a property of the purely linear circuit model and does not directly correspond to electrochemical polarization in a real electrode.

A.1.6 Influence of Interlayer

The influence of electrode inhomogeneity was investigated by introducing the 1 μm element shown in Figure A.1(d) with varying parameters. Assuming a 1 μm element with parameters from Case 1 (except layer thickness) represents layer A, from Case 2 represents layer B, and from Case 3 represents layer C.

To study the effect of a porous interlayer, the first four A layers in Case 1 were replaced by the higher-performing layer B (Case 10) or the lower-performing layer C (Case 11). The corresponding impedance spectra and DRTs are presented in Figure A.4(a,b), and the resulting resistances are summarized in Table A.2.

Table A.2: Simulation parameters for variation of interlayer and layer sequence.

Case	Layer Sequence	Total thickness (μm)	R_{pol} (Ω)	R_{ohm} (Ω)
10	BBBBAAAA	8	0.137	0.00199
11	CCCCAAAA	8	0.265	0.00199
12	ABABABAB	8	0.151	0.00199
13	ACACACAC	8	0.247	0.00199

The ohmic resistance shows no significant changes between the cases. In contrast, the polarization resistance differs among Cases 1, 10, and 11. Assuming that the GDC interlayer exhibits lower reactivity than the Ni/GDC layer, Case 11 shows a 33% increase in polarization resistance. If the Ni surface diffuses into the interlayer and activates the GDC surface, the polarization resistance would decrease. Thus, if the interlayer performs better than the assumed electrode,

an improvement may be observed, as in Case 10. This could explain the observed performance enhancement in V1.2 cells, as discussed in Section 4.4.1.1.

In the DRT spectra, peak P_1 decreases with decreasing charge transfer resistance in the layers near the electrolyte. This observation supports the findings of Dierickx (65), indicating that the reactivity near the electrolyte is the most critical. Since electron transport occurs several orders of magnitude faster than ionic transport, the reaction sites are confined to regions near the ion source. Changes in the side peaks are not pronounced.

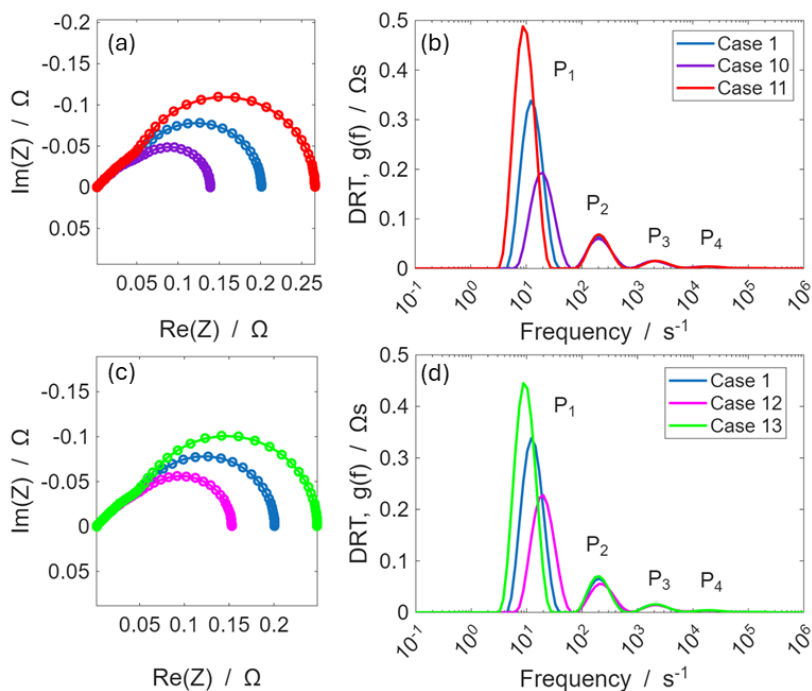


Figure A.4: The simulated impedances and corresponding DRTs regarding the impact of (a, b) the interlayer and (c, d) layer sequence. Legend corresponds to the first column of Table A.2.

A.1.7 Influence of Layer Sequence

In real electrodes, their behavior deviates from that of an ideal homogeneous layer. Thus, when describing the electrochemical performance using RQ elements, an index n is introduced to quantify the degree of deviation from ideality. This inhomogeneity was investigated by varying the layer sequence in the 8 μ m electrode, as listed in Cases 12 and 13 in Table A.2. The resulting impedance spectra and DRTs are shown in Figure A.4(c,d).

The polarization resistance decreases when better-performing layers B are interposed into the electrode, whereas the introduction of layer C leads to a deterioration in performance. The same trend is observed in the DRTs, where the peak P_1 decreases from Case 13 to Case 1 and then to Case 12. A slight decrease in P_2 is also present, as shown in Figure A.4(d). Comparing Case 1 with Cases 10–13 further highlights the importance of the layer adjacent to the electrolyte. Therefore, in this work, cells without interlayers were chosen for the AST and aging modeling, despite the positive impact of interlayers on overall performance.

A.2 Manufacturing Details for Tested Cells

In the following tables, the fabrication details of all cell variants are listed by fabrication technique. Further details can be found at the Forschungszentrum Jülich, Institute for Materials Synthesis and Manufacturing Processes (IMD-2), under the direction of Hon.-Prof. Dr.-Ing. Norbert H. Menzler.

Table A.3: Details in fabrication of screen-printed Ref1, V1, V2, V3 and V5 (Part 1).

Cell	Interlayer @1300 °C	Ni / GDC Electrode		Current Collector Layer			
		Thickness / μm	Recipe	Sinter T / °C	Thickness / μm	Particle size $d_{\text{Ni}}/d_{\text{NiO}}$ / μm	Thickness / μm
Variant							
Ref1	4	usual FZJ paste	1400	4	0.5		
V1.1	4	usual FZJ paste	1400	4	0.5		
V1.2	4	usual FZJ paste	1400	4	0.5	4	
V1.2b	0	usual FZJ paste	1400	8	0.5		
V1.2c	0	usual FZJ paste	1400	8	1.40	8	
V1.3	4	usual FZJ paste	1300	16	0.5	4	
V1.4a	0	usual FZJ paste	1300	8	0.5	4	
V1.4b	0	usual FZJ paste	1300	8	1.4	8	
V1.5a	0	usual FZJ paste	1200	8	0.5	4	
V1.5b	0	usual FZJ paste	1200	8	1.4	8	
V2	4	usual FZJ paste	1300	10	0.5	4	
V3.1	4	Fine particle paste 1	1400	-	0.5	4	
V3.2	4	Fine particle paste 1	1325	-	0.5	4	

Table A.4: Details in fabrication of screen-printed variants Ref1, V1, V2, V3 and V5 (Part 2, Continued).

Cell	Interlayer @1300 °C	Ni / GDC Electrode			Current Collector Layer	
Type	Thickness / μm	Recipe	Sinter T / $^{\circ}\text{C}$	Thickness / μm	Particle size $d_{\text{Ni}}/d_{\text{NiO}}$ / μm	Thickness / μm
V3.3	4	Literature-known / synthesized nanoparticles and literature-known / synthesized GDC nanoparticles 1:1	NiO 1200	-	0.5	
V3.4	4	Literature-known / synthesized nanoparticles and GDC nanoparticles from Fuelcell Materials 1:1	NiO 1200	-	0.5	
V3.5	4	Literature-known / synthesized nanoparticles and GDC fine particles (lower μm range from Fuelcell Materials 1:1)	NiO 1200	-	0.5	
V3.7	4	Paste mixture of nano-GDC and "normal" NiO	1400		0.5	4
V3.8	4	Cells composed of nano-NiO and "normal" GDC	1400		0.5	
V3.9	4	Original version of 3.1 with more solids phase	1400		0.5	
V3.10	4	Co-sintered V3.1	1400		0.5	
V3.11	4	Co-sintered V3.1	1300		0.5	
V3.12a	0	Fine particle paste 2	1400	8	1.4	8
V3.12b	0	Fine particle paste 2	1080		1.4	8
V3.12c	0	Fine particle paste 2	980		1.4	8
V5.1	4	"Fine" paste, grain size in the μm range	1350		0.5	4

Table A.5: Details in fabrication of variant V4 with electrode from Ni infiltrated into GDC skeleton.

Cell	Ni / GDC Electrode				Current Collector Layer		
	Type	GDC sinter $T / ^\circ\text{C}$	Thickness $/ \mu\text{m}$	Concentration $\text{Ni}(\text{NO}_3)_2(\text{aq})$ $/ \text{mol/L}$	Infiltration times	Particle size $d_{\text{Ni}}/d_{\text{NiO}}$ $/ \mu\text{m}$	Thickness $/ \mu\text{m}$
V4.1		1300			10	0.5	4
V4.2		1200			10	0.5	4
V4.3		1125			5	0.5	4
V4.4a		1200			1	1.4	8
V4.4a wo CC		1200			1	-	0
V4.4b		1200			2	1.4	8
V4.4b wo CC		1200			2	-	0
V4.4c		1200	8	3	3	1.4	8
V4.5a		1300			1	0.5	4
V4.5a wo CC		1300			1	-	0
V4.5b		1300			2	0.5	4
V4.5b wo CC		1300			2	-	0
V4.5c		1300			3	0.5	4
V4.5c wo CC		1300			3	-	0
V4.6		1200			2	0.5	4

Table A.6: Details in fabrication of variant V6 with electrode from GDC infiltrated into NiO skeleton.

Cell	GDC Interlayer		Ni / GDC Electrode			Current Collector Layer		
Type	$T_{\text{sinter}} / ^\circ\text{C}$	Thickness (after reduction) / μm	$T_{\text{sinter,Ni}} / ^\circ\text{C}$	Thickness (after reduction) / μm	$c_{\text{GDC}(\text{NO}_3)_2} / \text{mol/L}$	Infiltration times	$d_{\text{Ni}} / d_{\text{NiO}} / \mu\text{m}$	Thickness / μm
V6.1			1100	8	Supersaturated	9		
V6.2			1200	7	Supersaturated	9		
V6.3			1300	5	Supersaturated	9		
V6.4			1025	8	Supersaturated	5		
V6.5			1100	8	Supersaturated	5		
V6.6	1300	9	1200	7	Supersaturated	5	0.5	4
V6.7			1300	5	Supersaturated	5		
V6.8			1100	8	Supersaturated	10		
V6.9			1200	7	Supersaturated	10		
V6.10			1300	5	Supersaturated	10		
V6.11			1100	3	3	15		

A.3 Sample List

The cells investigated and presented in this work are summarized in Table A.7 to A.11. All cells are symmetrical electrolyte-supported cells with Ni/GDC electrodes.

In this study, the cell ID is defined as a composite label consisting of the test number and the cell variant (e.g., IS1-446_V1.2b). When multiple cells of the same variant are tested within a single assembly, the cell ID is designated as IS1-xxx_Vx.x_n, where n denotes the nth cell of variant Vx.x, numbered from the top of the assembly in test IS1-xxx.

Details of the fabrication parameters and cell components are provided in Tables A.3–A.6.

Table A.7: Cells used for validation of the novel multi-test method (Section 4.1).

Cell ID	Comment	Figures
IS1-454_V1.2b	After reduction at 650 °C and initial characterization separately, the cells were built into an assembly and operated at 700 °C in	3.1, 4.1, 4.32, 4.38
IS1-454_V1.5a	humidified hydrogen containing 50% water vapor for 880 h,	4.1, 4.2
IS1-454_V1.4a	afterwards with variations in hydrogen and steam partial pressure, alternating inert gas, and cooling down.	4.1, 4.10
IS1-456_V4.6	Reduced at 650 °C, initial characterization, operated at 750 °C with 50% humidity in hydrogen for 180 h, cooled down. In a multi-cell test setup, alternating inert gas at 600 °C, cooled down, demounting, rebuilt in a single-cell setup, heated up to 600 °C, alternating inert gas, cooled down.	4.3

Table A.8: Cells used to investigate the impact of fabrication parameters on initial performance (Section 4.2).

Cell ID	Comment	Figures
IS1-438_V6.5	Reduced at 650 °C, initial characterization, cooled down.	3.3, 4.14, 4.38
IS1-442_Ref1	Reduced at 650 °C, initial characterization, cooled down.	3.3, 4.27
IS1-442_V1.2	Reduced at 650 °C, initial characterization, cooled down.	3.3, 4.11, 4.37
IS1-444_V1.2	Reduced at 800 °C, initial characterization, cooled down.	3.1, 4.11
IS1-446_V1.2b	Reduced at 650 °C, initial characterization, cooled down.	4.9, 4.38
IS1-449_V4.4b	Reduced at 550 °C, initial characterization, cooled down.	4.13
IS1-449_V4.4c	Reduced at 550 °C, initial characterization, cooled down.	4.13
IS1-450_V4.4a	Reduced at 550 °C, initial characterization, cooled down.	4.13
IS1-454_V1.4b	Reduced at 650 °C, initial characterization, cooled down.	4.10
IS1-462_V4.5b	Reduced at 550 °C, initial characterization, cooled down.	3.3, 4.13
IS1-464_V3.12c	Reduced at 650 °C, initial characterization, cooled down.	4.12
IS1-465_V3.12b	Reduced at 650 °C, initial characterization, cooled down.	4.12
IS1-466_V3.12a	Reduced at 650 °C, initial characterization, cooled down.	4.12

Table A.9: Cells used to identify electrode loss mechanisms for the equivalent circuit model (Section 4.3).

Cell ID	Comment	Figure
IS1-437_V6.1	Reduced at 650 °C, initial characterization, operated at 900 °C with 50% steam in hydrogen for 650 h, process identification via variation of temperatures, hydrogen and steam partial pressure, cooled down.	4.15
IS1-441_V6.5	Reduced at 650 °C, initial characterization, operated at 700 °C with 50% steam in hydrogen for 1050 h, process identification via variation of hydrogen and steam partial pressure, alternating inert gas, cooled down.	4.15
IS1-469_V1.5a	Reduced at 650 °C, initial characterization, operated at 700 °C with 50% steam in hydrogen for 550 h, process identification via variation of temperatures, hydrogen and steam partial pressure, cooled down.	4.16
IS1-454_V1.4a	Reduced at 650 °C, initial characterization, operated at 700 °C with 50% humidity in hydrogen for 880 h, variation of hydrogen and steam partial pressure, alternating inert gas, cooled down.	4.16
IS1-479_V3.12b	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 600 °C with 50% steam in hydrogen for 1000 h, cooled down.	4.17
IS1-458_V4.5b	Reduced at 550 °C, initial characterization at 650 and 600 °C, operated at 600 °C with 50% steam in hydrogen for 1000 h, cooled down.	4.17

Table A.10: Cells tested under elevated stress conditions for initial degradation assessment and AST protocol design (Section 4.4).

Cell ID	Comment	Figures
IS1-427_V1.2_1	Reduced at 800 °C, initial characterization, cooled down.	4.22, 4.23, 4.37
IS1-424_V1.2_1	Reduced at 800 °C, initial characterization, operated at 900 °C with 50% steam in hydrogen for 240 h, cooled down.	4.19, 4.22, 4.23, 4.37
IS1-429_V1.2_1	Reduced at 800 °C, initial characterization, operated at 900 °C with 50% steam in hydrogen for 1,100 h, cooled down.	4.19-4.21, 4.24, 4.31, 4.37
IS1-430_V6.1	Reduced at 800 °C, initial characterization, operated at	4.35
IS1-430_V6.2	900 °C with 50% steam in hydrogen for 830 h, cooled	4.35
IS1-430_V6.3	down.	4.35
IS1-437_V6.1	Reduced at 650 °C, initial characterization, operated at 900 °C with 50% steam in hydrogen for 650 h, process	4.34, 4.35, 4.36, 4.38
IS1-437_V6.3	identification via variation of temperatures, hydrogen and steam partial pressure, cooled down.	4.35
IS1-441_V6.4	Reduced at 650 °C, initial characterization, operated at	4.35
IS1-441_V6.5	700 °C with 50% steam in hydrogen for 1050 h, process	4.33, 4.35, 4.36, 4.38
IS1-441_V6.6	identification via variation of hydrogen and steam partial pressure, alternating inert gas, cooled down.	4.35
IS1-441_V6.7		4.35
IS1-443_Ref1		4.26, 4.27, 4.31, 4.37
IS1-443_V1.2	Reduced at 650 °C, initial characterization, operated at 800 °C with 50% steam in hydrogen for 953 h, cooled	4.28, 4.29, 4.31
IS1-443_V6.11_1	down.	4.35
IS1-443_V6.11_2		4.35
IS1-443_V6.11_3		4.35
IS1-445_V1.2	Reduced at 650 °C, initial characterization, operated at	4.30, 4.31
IS1-445_V6.11_1	800 °C with 10% steam in hydrogen for 390 h, cooled	4.35
IS1-445_V6.11_2	down.	4.35
IS1-448_V1.2b_1	Reduced at 650 °C, initial characterization, operated at	4.32, 4.38
IS1-448_V1.2b_2	600 °C with 50% steam in hydrogen for 130 h, cooled down. After demounting one cell, reheated up to nominal condition and further operated to 550 h, cooled down.	4.31, 4.32, 4.38
IS1-456_V1.2	Reduced at 650 °C, initial characterization, operated at	4.31
IS1-456_V1.2b	750 °C with 50% steam in hydrogen for 180 h, cooled	4.31
IS1-456_V1.2c	down.	4.31
IS1-470_V1.5a	Reduced at 650 °C, initial characterization, operated at 900 °C with 50% steam in hydrogen for 130 h, cooled down.	4.25, 4.31

Table A.11: Cells from variant V1.5a employed for accelerated stress testing (AST) and aging modeling of Ni/GDC anodes (Section 4.5).

Cell ID	Comment	Figures
IS1-471_V1.5a	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 750 °C with 50% steam in hydrogen for 450 h, cooled down	4.39, 4.40, 4.42-4.53
IS1-481_V1.5a_1	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 725 °C with 50% steam in hydrogen for 480 h, cooled down	4.40, 4.42-4.53
IS1-469_V1.5a	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 700 °C with 50% steam in hydrogen for 550 h, process identification via variation of temperatures, hydrogen and steam partial pressure, cooled down	4.39, 4.40, 4.42-4.53
IS1-478_V1.5a	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 650 °C with 50% steam in hydrogen for 590 h, cooled down	4.39, 4.40, 4.42-4.53
IS1-483_V1.5a_1	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 625 °C with 50% steam in hydrogen for 2700 h, cooled down	4.41-4.53
IS1-479_V1.5a	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 600 °C with 50% steam in hydrogen for 1000 h, cooled down	4.39, 4.40, 4.42-4.53
IS1-474_V1.5a	Reduced at 650 °C, initial characterization at 650 and 600 °C, cooled down	4.9, 4.40, 4.42, 4.44
IS1-480_V1.5a	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 600 °C with 30% steam in hydrogen for 800 h, cooled down	4.39, 4.42, 4.44, 4.46, 4.47
IS1-475_V1.5a	Reduced at 650 °C, initial characterization at 650 and 600 °C, operated at 600 °C with 10% steam in hydrogen for 780 h, cooled down	4.39, 4.42, 4.44, 4.46, 4.47

A.4 MATLAB Code for Simulating Pseudo-Inductive Loop

The code for the simulation in Section 4.1.3 is listed below. This is an example of the impedance at 700 °C in an atmosphere of 5% humidity, 50% hydrogen, and 35% inert gas.

Listing A.1: Simulation of pseudo-inductive loop impedance.

```
%% circuit-based
syms I w t R1 C1 R2 R3 F C2 C3
IR1=I*(1/R1)/(1/R1+1i*w*C1)*exp(1i*w*t);
IR2=I*(1/R2)/(1/R2+1i*w*C2)*exp(1i*w*t);
IR3=I*(1/R3)/(1/R3+1i*w*C3)*exp(1i*w*t);
Z2=2*R2/(1+1i*w*R2*C2);
%electrode B.2
delta_m1_B2=IR1/2/F;
delta_m1_B2_H2=int(delta_m1_B2,t);
delta_m1_B2_H2O=-delta_m1_B2_H2;
%electrode C.1
delta_m2_C1=IR2/2/F;
delta_m2_C1_H2O=int(delta_m2_C1,t);
delta_m2_C1_H2=-delta_m2_C1_H2O;
%electrode C.2
delta_m2_C2=IR2/2/F;
delta_m2_C2_H2O=-int(delta_m2_C2,t);
delta_m2_C2_H2=-delta_m2_C2_H2O;
%electrode D.1
delta_m3_D1=IR3/2/F;
delta_m3_D1_H2O=int(delta_m3_D1,t);
delta_m3_D1_H2=-delta_m3_D1_H2O;
%% the atmosphere
% gas at standard conditions is 22.4 L/mol
syms T R P0 A d pH2 pH2O
Vm_T=R*T/P0;
% space between two electrodes
V=A*d/2;
m_set_H2=V/Vm_T*pH2;
m_set_H2O=V/Vm_T*pH2O;
```

```

m_12_H2=m_set_H2+delta_m1_B2_H2+delta_m2_C1_H2 ;
m_12_H2O=m_set_H2O+delta_m1_B2_H2O+delta_m2_C1_H2O ;
m_23_H2=m_set_H2+delta_m2_C2_H2+delta_m3_D1_H2 ;
m_23_H2O=m_set_H2O+delta_m2_C2_H2O+delta_m3_D1_H2O ;
%% Spannungunterschiede
delta_U2=-R*T/2/F*log ( m_12_H2O*m_23_H2 / m_12_H2 / m_23_H2O );
%% calculate impedance
U_cell=I*exp(1 i*w*t)*Z2;
Umess=U_cell+delta_U2 ;
Z_mess=Umess/( I*exp(1 i*w*t) );
%% simulate H2O 5%
% I
figure
% default I
a=0.05;
% R1 C1 R2 R3 F C2 C3
z=0.44;e=0.09;f=0.15; c=0.25; g=96485; c2=0.018; c3=0.33;
%T R P0
h=973.15; y=8.314; j=101325;
% A d pH2 pH2O
k=1e-4; l=200e-6; m=0.5; n=0.05;
% the measurement frequency point
Z_cal=subs (Z_mess , [ I ,R1 ,C1 ,R2 ,R3 ,F ,T ,R ,P0 ,A ,d ,pH2 ,pH2O ,C2 ,C3 ] ,
[ a ,z ,e ,f ,c ,g ,h ,y ,j ,k ,l ,m ,n ,c2 ,c3 ] );
% w
b=[1.19533e+04 9.86050e+03 8.13414e+03 6.71002e+03 5.53524e+03
4.56614e+03 3.76670e+03 3.10723e+03 2.56322e+03 2.11446e+03
1.74426e+03 1.43888e+03 1.18696e+03 9.79148e+02 8.07720e+02
6.66305e+02 5.49650e+02 4.53418e+02 3.74034e+02 3.08548e+02
2.54528e+02 2.09966e+02 1.73205e+02 1.42881e+02 1.17865e+02
9.72295e+01 8.02067e+01 6.61642e+01 5.45802e+01 4.50244e+01
3.71416e+01 3.06389e+01 2.52747e+01 2.08496e+01 1.71993e+01
1.41881e+01 1.17040e+01 9.65489e+00 7.96453e+00 6.57011e+00
5.41982e+00 4.47092e+00 3.68816e+00 3.04244e+00 2.50977e+00
2.07037e+00 1.70789e+00 1.40887e+00 1.16221e+00 9.58730e-01
7.90880e-01 6.52410e-01 5.38190e-01 4.43960e-01 3.66230e-01
3.02110e-01 2.49220e-01 2.05590e-01 1.69590e-01 1.39900e-01
1.15410e-01 9.52000e-02 7.85300e-02 6.47800e-02 5.34400e-02

```

```
4.40900e-02 3.63700e-02 3.00000e-02];  
parfor no=1:length(b)  
    Z_cal_real=subs(Z_cal,w,b(no));  
    Z_real(no)=int(Z_cal_real,0,2*pi/b(no))/(2*pi/b(no));  
    REAL(no)=real(Z_real(no));  
    IMAG(no)=imag(Z_real(no));  
end  
plot(REAL,IMAG,'o-r');
```

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