

OVE KORJUS

The development
of ceramic fuel electrode
for solid oxide cells



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TABLE OF CONTENTS

1. LIST OF ORIGINAL PUBLICATIONS	7
2. ABBREVIATIONS AND SYMBOLS	8
3. INTRODUCTION	11
4. LITERATURE OVERVIEW	13
4.1. Solid oxide cells	13
4.2. Ni-cermet fuel electrodes	14
4.3. Ceramic fuel electrodes	15
4.3.1. LaCrO _{3-δ} -based materials	15
4.3.2. SrTiO _{3-δ} -based materials	17
4.3.3. Surface activation by particle ex-solution	19
4.4. Factors influencing the cell voltage	19
4.5. Electrochemical impedance spectroscopy	21
4.5.1. Equivalent circuit fitting	24
4.6. X-ray diffraction	25
5. EXPERIMENTAL	28
5.1. Preparation of single cells	28
5.2. Electrochemical measurements	31
5.3. Physical characterization of the materials	33
5.3.1. <i>operando</i> and <i>in situ</i> XRD measurements	33
6. RESULTS AND DISCUSSION	36
6.1. Ni-GDC model system <i>operando</i> XRD measurements data	36
6.2. Stability of La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.3} Ni _{0.2} O _{3-δ} electrodes	40
6.2.1. Electrochemical stability tests of nonporous PLD electrode ...	45
6.2.2. Influence of the redox cycle on the performance of the La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.3} Ni _{0.2} O _{3-δ} electrode	46
6.2.3. <i>Operando</i> EC-HT-XRD in fuel cell mode	48
6.3. La _{0.25} Sr _{0.25} Ca _{0.4} Ti _{1-x} Ni _x O _{3-δ} SOC fuel electrode	53
6.3.1. Physical characterization	53
6.3.2. Electrochemical analysis	60
6.3.3. Electrochemical characterization of La _{0.25} Sr _{0.25} Ca _{0.4} Ti _{0.95} Ni _{0.05} O _{3-δ} fuel electrode in 2-electrode button cell	65
7. SUMMARY	67
8. REFERENCES	69
9. SUMMARY IN ESTONIAN	74
10. ACKNOWLEDGEMENTS	76
11. PUBLICATIONS	77

CURRICULUM VITAE	139
ELULOOKIRJELDUS	140

1. LIST OF ORIGINAL PUBLICATIONS

- I. O. Korjus, J. Aruväli, I. Kivi, M. Kodu, E. Lust, G. Nurk, Simultaneous *Operando* Characterization of Crystallographic and Electrochemical Properties of Ni-Ce_{0.9}Gd_{0.1}O_{2-δ} Solid Oxide Fuel Cell Anode. J. Electrochem Soc., 165 (13) (2018) F1043–F1050. DOI: 10.1149/2.0281813jes.
- II. O. Korjus, J. Aruväli, P. Paiste, K. Kooser, S. Granroth, H. Mändar, M. Kodu, R. Härmas, M. Ainsar, E. Lust, G. Nurk, Study of Electrochemical and Crystallographic Changes During Initial Stabilisation of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.3}Ni_{0.2}O_{3-δ} Reversible Solid Oxide Cell Electrode. Fuel Cells, 20 (6) (2020), 741–752. DOI: 10.1002/fuce.202000104.
- III. O. Korjus, P. Möller, K. Kooser, T. Käämbre, O. Volobujeva, J. Nerut, S. Kotkas, E. Lust, G. Nurk, Influence of Ni Concentration on Electrochemical and Crystallographic Properties of La_{0.25}Sr_{0.25}Ca_{0.4}Ti_{1-x}Ni_xO_{3-δ} Solid Oxide Fuel Cell Anode, J. Power Sources, (2021). DOI: 10.1016/j.jpowsour.2021.229739
- IV. O. Korjus, I. Kivi, J. Aruväli, K. Kirsimäe, G. Nurk, In *Operando* Electrochemical High-Temperature X-Ray Diffraction Study of Ni-Ce_{0.9}Gd_{0.1}O_{2-δ} Redox Properties, ECS Trans. 78 (1) (2017) 1139–1148. DOI: 10.1149/07801.1139ecst.
- V. O. Korjus, G. Nurk, J. Aruväli, I. Kivi, M. Maide, E. Lust, Electrochemical- and Crystallographic *Operando* Characterization of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.3}Ni_{0.2}O_{3-δ} Anode Infiltrated into Sc_{0.2}Ce_{0.01}Zr_{0.79}O_{2-δ} Electrolyte Scaffold. ECS Trans. 91 (1) (2019) 1683–1692. DOI: 10.1149/09101.1683ecst.

Author's contribution:

- Paper I: Performed the synthesis of single cells, all physical and all electrochemical characterization of the single cells, and analysis of the data. Mainly responsible for the preparation of the manuscript.
- Paper II: Performed the synthesis of single cells, some physical and all electrochemical characterization of the single cells, and analysis of the data. Mainly responsible for the preparation of the manuscript.
- Paper III: Performed the synthesis of single cells, some physical and all electrochemical characterization of the single cells, and analysis of the data. Mainly responsible for the preparation of the manuscript.
- Paper IV: Performed the synthesis of single cells, all physical and all electrochemical characterization of the single cells, and analysis of the data. Mainly responsible for the preparation of the manuscript.
- Paper V: Performed the synthesis of single cells, some physical and all electrochemical characterization of the single cells, and analysis of the data. Mainly responsible for the preparation of the manuscript.

2. ABBREVIATIONS AND SYMBOLS

$p_{H_2O}^f$	partial pressure of H ₂ O in the fuel electrode compartment
$p_{H_2}^f$	partial pressure of H ₂ in the fuel electrode compartment
$p_{O_2}^a$	partial pressure of oxygen in the air electrode compartment
A	Constant phase element pre-exponent coefficient
$A(Ni)_{max}$	maximum area of Ni(111) Bragg peak
$A(Ni)_t$	area of Ni(111) Bragg peak at a fixed measurement time
$A(NiO)_{max}$	maximum area of NiO(200) Bragg peak
$A(NiO)_t$	area of NiO(200) Bragg peak at a fixed measurement time
AC	alternating current at a certain time
a	lattice parameter (1 of 6)
a_{LSCMN}	lattice parameter of LSCMN (1 of 2 non-constant ones)
a_{ScCeSZ}	lattice parameter of ScCeSZ (only non-constant one)
AV	alternating voltage
C	sum of corrections in the relationship between F_{hkl} and I_{hkl}
CE	counter electrode
CeLSCM	Ce _{0.1} La _{0.65} Sr _{0.25} Cr _{0.5} Mn _{0.5} O _{3-δ}
c_{LSCMN}	lattice parameter of LSCMN (1 of 2 non-constant ones)
CNLS	Complex Nonlinear Least Squares
CPE	constant phase element
d	distance between lattice planes
E	potential
E^0	standard potential
E_a	activation energy
$E_{a,Rp}$	activation energy calculated from polarization resistance
$E_{a,Rs}$	activation energy calculated from series resistance
E_0	alternating voltage amplitude
E_{0p-p}	alternating voltage peak to peak amplitude
EC	electrolysis cell
E_{cell}	cell potential
EIS	electrochemical impedance spectroscopy
F	Faraday constant
f	alternating voltage frequency
FC	fuel cell
F_{hkl}	structure factor
f_{max}	relaxation frequency
FWHM	full width half maximum
GDC	gadolinia doped ceria
GI-XRD	grazing incidence X-ray diffraction
HT	high temperature
i	current density
$I(t)$	current as a function of time

I_0	alternating current amplitude
I_{0p-p}	alternating current peak to peak amplitude
ICP-MS	inductively coupled plasma mass spectrometry
I_{hkl}	integral intensity of a Bragg peak with plane indices hkl
K	Scherrer constant
L	inductance
LSC	$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$
LSCM	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$
LSCMN	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$
LSCNT-2	$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.98}\text{Ni}_{0.02}\text{O}_{3-\delta}$
LSCNT-5	$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$
LSCNT-10	$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$
LSCNT-20	$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$
LSCNT-x	$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$
LSCT	$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{TiO}_{3-\delta}$
LSCT _{A-}	$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{TiO}_{3-\delta}$, emphasizing that it has a-site deficiency
LST	$\text{La}_{1-x}\text{Sr}_x\text{TiO}_{3-\delta}$
M	multiplicity factor
MIEC	mixed ion-electron conductor
n	integer number
OCV	open-circuit voltage
P	power density
p	true crystallite size
PLD	pulsed-laser deposition
p_{O_2}	oxygen partial pressure
p_{H_2}	hydrogen partial pressure
R	ideal gas constant
R	resistance
RC-element	equivalent circuit consisting of a resistor in parallel with a capacitor
-R-CPE-	equivalent circuit consisting of a resistor in parallel with a CPE
RE	reference electrode
R_p	polarization resistance
R_s	series resistance
ScCeSZ	scandia and ceria stabilized zirconia
SDC	samaria doped ceria
SEM	scanning electron microscopy
SOC	solid oxide cell
SOEC	solid oxide electrolysis cell
SOFC	solid oxide fuel cell
T	temperature
t	time
TGA	thermogravimetric analysis
TOF-SIMS	time-of-flight secondary ion mass spectrometer

TPB	triple phase boundary
$V(t)$	voltage as a function of time
V_0	alternating voltage amplitude value
WE	working electrode
XRF	X-ray fluorescence spectrometry
YSZ	yttria stabilized zirconia
Z	impedance
$ Z $	magnitude of impedance vector
Z'	real part of the impedance
Z''	imaginary part of the impedance
$Z(\omega)$	impedance with emphasis that it is a function of angular frequency
$Z(\omega)'$	real part of the impedance with emphasis that it is a function of angular frequency
$Z(\omega)''$	imaginary part of the impedance with emphasis that it is a function of angular frequency
Z_{arc}	impedance of RC-element
Δ^2	weighted sum of squares
$\varphi(\omega)$	phase shift with emphasis that it is a function of angular frequency
χ^2	chi-squared (distribution)
ΔG	reaction free energy change
α_{CPE}	fractional exponent in CPE
β	integral breadth
ε	lattice strain
λ	wavelength of the incident beam
θ	diffraction angle
τ_{RC}	time constant of RC-element
ω	angular frequency
ϕ	angle of incidence

3. INTRODUCTION

Tackling climate change is one of the challenging yet vital problems of modern society. To reduce the CO₂ emissions, it is necessary to provide an alternative to classical coal-fired (or oil shale fired) thermal power stations. Solid oxide cells (SOC) can be useful in several ways in this field. Firstly, in a solid oxide electrolysis cell (SOEC) mode, the cell would be able to efficiently convert surplus electric energy from intermittent energy sources like wind and solar to fuels. Secondly, in a solid oxide fuel cell (SOFC) mode, the cell would be able to convert chemical energy back to electrical energy with high efficiency when electricity demand is high. Even as a standalone (without emphasizing the need for renewable sources) technology, the solid oxide cells are getting more competitive in the energy conversion market [1–5].

State of the art SOC fuel electrodes are Ni-cermets – materials that consist of metallic nickel mixed with ceramic oxide, usually yttria-stabilized zirconia (YSZ) or gadolinia doped ceria (GDC). Ni is an excellent electronic conductor, catalytically active towards fuel oxidation and quite affordable [6,7]. However, it also has several challenges. Ni oxidation to NiO, which might ruin the electrodes' microstructure and is less conductive, takes place at working conditions if oxygen partial pressure (p_{O_2}) rises above a threshold level (depends on temperature) in the fuel electrode compartment (leakage or too heavy working load) [8–10]. Metallic Ni is also prone to sulphur poisoning [11,12] and coking [13] if carbonaceous fuel without enough steam is used. Even if gases are purified from sulphur, and the correct steam to carbon ratio is used, metallic Ni still has a tendency to coarsen over time, which leads to performance losses [14,15].

Therefore an effort to find suitable alternatives to metal-ceramic electrodes has been made. One of the most attractive solutions is the application of ceramic mixed ion-electron conductor (MIEC) materials. These materials have potentially fewer problems with stability (coarsening, sulphur poisoning and coking). Some of these materials are stable (no significant changes in oxygen stoichiometry) in both reducing and oxidative atmospheres, which means that small changes in the fuel compartment's p_{O_2} do not have devastating effects on the electrode's microstructure [16,17].

Perovskite structure is a promising choice for the ceramic electrode material since it is highly flexible and can tolerate various cations in the crystal lattice; hence it is possible to tailor the material properties needed for high performance and stability with appropriate metal cation substitutions [18,19].

However, it is very tricky to predict how specific element substitution changes the electrode's catalytic activity and crystallographic properties at working conditions. Moreover, it is not even straightforward to correlate *ex-situ* measured crystallographic data with the electrochemical analysis results. Therefore, it is challenging to understand why some substitutions result in better-performing electrodes than others without in situ measurements. Still, it is vital to

know how the changes taking place in the crystal structure affect cell performance and stability to design new advanced materials.

This work aims to develop a perovskite-based stable and catalytically active full ceramic fuel electrode for SOCs. A deeper understanding of the relation of the fuel electrode's electrochemical characteristics and crystallographic parameters is necessary for designing materials with needed properties. This work has exploited various *ex-situ* and *in-situ* methods to understand why some materials are less stable and underperforming. Moreover, the electrochemical high temperature operando XRD method has been developed and applied to understand processes in working SOC. This thesis has mainly focused on a detailed analysis of two ceramic materials – one is LaCrO_3 -based and the other SrTiO_3 -based.

4. LITERATURE OVERVIEW

4.1. Solid oxide cells

Solid oxide cells can operate in two modes – fuel cell and electrolysis mode (Fig. 1). The fuel cell mode is used to convert chemical energy from fuels to electricity and heat. To do the reverse process – generate fuels from electricity, solid oxide electrolyzers are used. Theoretically, it is possible to use the same cell in both modes. However, the systems are usually not well optimized to operate in both modes [3,4,6,20–22].

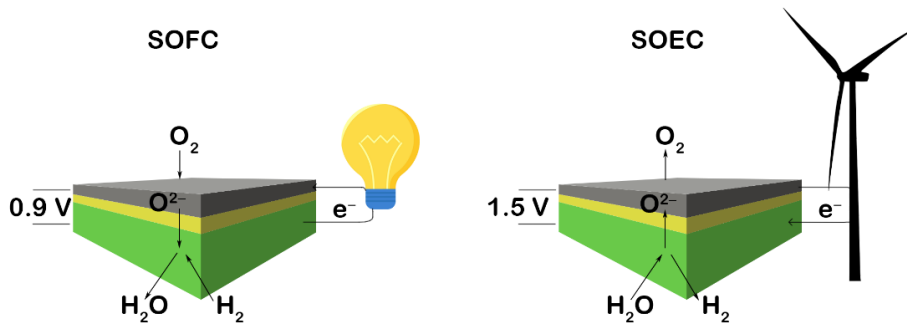


Figure. 1 Sketch of the principle of solid oxide cells in both fuel cell and electrolysis modes. The bottom green layer is a porous fuel electrode; the middle yellow is a dense ion-conducting electrolyte; the dark grey top layer is a porous cathode.

The classification and names of fuel cells (FC) and electrolysis cells (EC) come from the electrolyte, e.g. in SOFC and SOEC, the electrolyte material is a solid oxide. Like in other types of FCs/ECs, the electrolyte needs to be ion conductive, electronically non-conductive and has to separate electrodes and different gas atmospheres. The use of solid electrolyte in SOC systems eliminates the problems related to liquid electrolyte management. Since there are no moving parts in SOC systems (except air blowers), it also has a low maintenance cost. Compared to its low-temperature alternatives, SOC systems are more efficient and do not need any other fuel electrode catalyst than the electrode itself. SOFCs can also use various fuels that lower temperature cells cannot, like CO, hydrocarbons, alcohols and synthetic gas [6,7,20–24].

In SOC systems, there are mostly two main options for oxide conducting electrolytes – CeO₂-based and ZrO₂-based electrolytes. Doped CeO₂ electrolytes, like Sm_{0.2}Ce_{0.8}O_{2-δ} (SDC) and Gd_{0.2}Ce_{0.8}O_{2-δ} (GDC), become slightly electronically conductive in low p_{O_2} atmospheres and at a high temperature which leads to a drop in open circuit voltage (OCV) value if CeO₂-based electrolyte is used. The second problem with mentioned electrolytes is their fragility. So, if GDC/SDC electrolytes are used at all as a standalone electrolyte, they are operated at lower temperatures (<600 °C) since the OCV drop is less pronounced there [6,24,25].

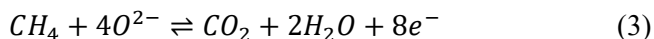
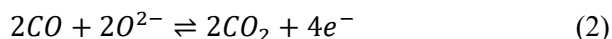
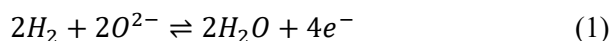
Zirconia-based electrolytes are by far the most common. Yttria-stabilized zirconia (YSZ) is the mainstream choice for SOC electrolyte due to its good conductivity at high temperatures and affordability. Scandia and ceria stabilized zirconia (ScCeSZ) is also quite widely used due to its higher conductivity at moderate temperature. However, it is relatively more expensive [6,7,24].

The general requirements for a SOC electrode material include excellent catalytic activity toward the reaction it governs, fuel oxidation in the fuel electrode and oxygen reduction reaction in the case of the air electrode. The electrode material also needs to be chemically compatible with the electrolyte and stable during the fabrication process and operation. The electrode needs to have sufficiently good mechanical strength and flexibility and a similar thermal expansion coefficient to the electrolyte. Finally, it also needs to be affordable [6,7,24,26].

4.2. Ni-cermet fuel electrodes

Fuel electrodes, where NiO is mixed with electrolyte material (GDC, YSZ, ScCeSZ), are called Ni-cermets. The NiO is reduced to Ni in the fuel atmosphere at high temperatures, providing electrodes with excellent electronic conductivity. Ni also promotes the possibility of internal reforming of hydrocarbons, making it possible to use them as fuel. The electrodes' necessary ionic conductivity comes from the mixed electrolyte material [6,7,24,26].

The reactions in Ni-cermet electrodes (Eq. 1, 2 and 3) can only take place in the triple-phase boundary (TPB) – the boundary between connected electrolyte particles, connected Ni-particles and the gas phase. If the particles are not connected, then they cannot provide pathways for electronic conduction (Ni-particles) and/or oxide ion conduction (electrolyte material particle). Hence, it cannot work as an active reaction site [6,7].



The Ni-particles at high temperatures over a while tend to minimize their surface energy with coarsening and taking spherical shape, leading to a decrease in the electrode's electronic conductivity. However, the Ni electronic conductivity is still excellent even after coarsening (410 S cm^{-1} at 900°C) [14], but coarsening still leads to a decrease in active TPB length, which leads to a loss in electrochemical performance [27].

Ni-catalyst is also prone to coke formation (when hydrocarbons are used as a fuel) and intolerance to some inorganic impurities [11,28–30]. One of the major problems lies with sulphur poisoning since most hydrocarbon fuels contain it and the complete removal of it is a costly process. Some methods

increase the Ni resistance to poisons, for example, creating Ni/gold alloys with magnetron sputtering [31,32]. However, these methods are still costly.

Coking takes place if dry hydrocarbons are feed directly to the fuel electrode. Steam reforming is used to avoid it. However, since relatively high concentrations (depending on temperature) of steam are necessary (usually steam to carbon ratio is set to 2:1), the fuel gets diluted and p_{O_2} increases, which leads to a decrease in efficiency and catalytic activity [16,33,34].

One of the most significant challenges for using Ni-ceramics is its stability at high temperature against oxidation in the air. However, volume changes taking place during successive cyclic reduction and oxidation (redox cycles) may be detrimental to the fuel electrode unity. The shrinkage of NiO particles during reduction is ~40%, and the increase of volume during oxidation of Ni is ~66%. This might be vital in fuel electrode-supported cells, where the redox cycles might lead to electrolyte cracking. The Ni-oxidation can occur due to accident (problems with fuel supply, leakage in seals) or under high fuel utilization conditions, where the p_{O_2} can locally increase above critical levels [8,9,35,36].

4.3. Ceramic fuel electrodes

The search for alternative fuel electrode materials to Ni-cermets is very active in the SOC field due to the reasons mentioned in the previous paragraph. Full ceramic anodes are envisaged as far more redox stable materials when compared to metal-cermets – there is no immense expansion relating to metal oxidation. Many oxides are stable in both oxidizing and reducing atmospheres, with only slight oxygen stoichiometry changes taking place when the atmosphere is switched from oxidizing to reducing. Thus, for a limited number of materials, only minor volume changes occur when switching between gas atmospheres [9,16,26].

Some of these electrodes have shown fewer problems with particle coarsening, sulfur poisoning, and carbon deposition in comparison with the fuel electrodes containing metallic Ni. One of the most significant advantages of MIEC material is the fact that reaction sites are not only on TPB. The fuel oxidation can occur in the whole gas-solid interface in these materials compared to Ni-cermets, where the reaction can only happen in the TPB region [16,37].

MIEC materials can have different crystal structures. However, the most prominent ones seem to be perovskites (ABO_3). This structure is highly flexible in the sense of tolerating various cations in the crystal lattice; hence it is possible to tailor the material properties with appropriate metal cation substitutions [16].

4.3.1. $LaCrO_{3-\delta}$ -based materials

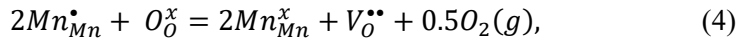
$LaCrO_{3-\delta}$ are used as SOC interconnect materials since they have excellent chemical stability in both oxidizing and reducing atmospheres [17,38,39]. In

principle, $\text{LaCrO}_{3-\delta}$ -based materials could also be used as SOC electrodes. However, without increasing conductivity, the active area where reaction could take place would be limited. Thus, the polarization resistance (R_p) of the electrode would be too high. Numerous studies have been published about substituting elements of this material with various dopants to decrease its R_p . The A-site is usually doped with Sr and B-site with different elements like Mn, Ni, Fe, Co, Ga, etc. [40–43]. One material that has shown comparable performance to Ni-cermets and has shown to be more resistant to coking is $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSCMN) [17,43].

As mentioned in the previous paragraph, one of the indicators for the chemical stability of the electrode is its chemical suitability with the electrolyte material (lack of interfacial reaction between electrode and electrolyte). Tao and Irvine [44] have shown with XRD measurements that no new phases have formed during sintering zirconia and $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) together at 1300 °C in air. However, surprisingly studying a slightly modified version of LSCM, $\text{Ce}_{0.1}\text{La}_{0.65}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (CeLSCM), Lay et al. [45] showed the formation of SrZrO_3 in the Ar atmosphere at 1250 °C. From these results, it could be concluded that the stability of the material and Sr-mobility are heavily dependent on the exact chemical composition and stoichiometry of the material.

There has been extensive research to evaluate LSCM-based materials stability in different p_{O_2} atmospheres. Zha et al. [46] reported only 1% volume difference between oxidized and reduced (pure H_2 atmosphere at 950 °C) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.45}\text{Mn}_{0.55}\text{O}_{3-\delta}$ at room temperature. However, this result does not mean that there is not more significant volume change at SOC working temperature, so this result might not mean much. Lay et al. [45] observed an increase in CeLSCM lattice parameters when the p_{O_2} of the sample gas atmosphere was changed from high to low p_{O_2} . They proposed that this effect is related to the reduction of the manganese oxidation state, which was accompanied by an increase of oxide ion vacancies. However, this phenomenon was not observed in the case of LSCM with thermogravimetric analysis (TGA) when the gas atmosphere was switched from air to the Ar [47]. Surprisingly, Bossch and McIntosh [48] showed 4.4% weight loss in the case of LSCMN when the gas atmosphere was changed from N_2 to 5% H_2 , 95% N_2 mixture. From these results, it could be concluded that the oxide ion vacancies start forming only at very low p_{O_2} atmosphere.

LSCM is a p-type electron conductor, which means that its electronic conductivity is higher in O_2 rich atmospheres and is decreased in a fuel atmosphere eq. 4 [45,49,50].



where $Mn_{Mn}^{\bullet}$ is Mn^{4+} positioned in the Mn^{3+} lattice site, O_O^x is neutral oxide ion positioned in its lattice site, Mn_{Mn}^x is Mn^{3+} sitting in its lattice site and $V_O^{\bullet\bullet}$ is oxide ion vacancy.

During the reduction of Mn^{4+} to Mn^{3+} , the lattice parameter increases due to two main reasons. Firstly, the oxide ion vacancies are formed to compensate for the change in lattice charge resulting from manganese reduction. Secondly, the reduction is accompanied by increased Mn-O-Mn length, leading to a somewhat lower electronic conductivity of the material [44,51,52].

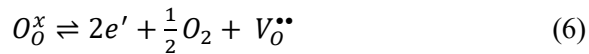
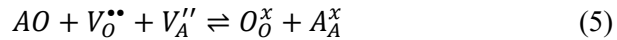
Unfortunately, only a limited amount of information is available in the literature about LSCM-based materials stability and degradation behaviour. Lu and Zhu [53] reported a 40 h stability test in the fuel cell mode, where they observed LSCM linear degradation, which they believed to be related to particle coarsening. A significant increase in the LSCM series resistance (R_s) in the electrolysis mode was reported by Xing et al. [54]. In co-electrolysis mode, Yoon et al. [55] reported a 1.21 times increase in the R_p after 40 h of cell operation at 0.5 A cm^{-2} . However, R_s did not change in their experiment.

The lack of stability information on LSCM-based materials in most papers and a few studies where degradation has been addressed makes it evident that instability problems are ignored in several cases. Thus, detailed research about LSCM-based materials is necessary.

4.3.2. $\text{SrTiO}_{3-\delta}$ -based materials

$\text{SrTiO}_{3-\delta}$ -based materials are promising MIECs to be considered as SOC electrodes. There are different ways to improve the n-type electronic conductivity of these materials. One way is to dope the material's A-site with donor dopant like La^{3+} . $\text{La}_{1-x}\text{Sr}_x\text{TiO}_{3-\delta}$ (LST) materials have demonstrated excellent n-type electron conductivity at SOC fuel electrode working conditions (80 – 360 S/cm at 1000 °C and in reducing atmosphere) [56,57].

Another way to improve its electronic conductivity is to create A-site vacancies to the perovskite lattice ($\text{A}_{1-x}\text{BO}_{3-\delta}$). High n-type conductivity in reducing atmospheres can be explained by the formation of free electrons, described by the following equations [58]:



Creating A-site deficiency into lattice leads to the formation of A-site vacancies ($V_{\text{A}}^{\prime\prime}$), which according to Le Chatelier' principle, shifts the equilibria (eq. 5) to the right. Thus, the amount of oxide ion vacancies is also decreased. The increase in O_{O}^x and the decrease in the concentration of $V_{\text{O}}^{\bullet\bullet}$ lead to the shift of equilibrium of the eq. (6) to the direction of facilitated removal of lattice oxygen, the formation of oxide ion vacancies and associated generation of free electrons. Another potential positive aspect accompanying A-site deficiency is the suppression of Sr segregation to surface and mobility [59,60].

There is also a possibility to improve electronic conductance by reducing the unit cell volume. Substituting Sr^{2+} ion with smaller Ca^{2+} cation forming $\text{La}_{0.2}\text{Sr}_{0.7-x}\text{Ca}_x\text{TiO}_{3-\delta}$ ($\text{LSCT}_{\text{A-}}$) for example, leads to a decrease in the unit cell volume and an increase in electronic conductivity if $x \leq 0.45$ [61]. $\text{LSCT}_{\text{A-}}$ has high electronic conductivity (27.53 S cm^{-1} at 900°C in $p_{\text{O}_2}=10^{-19}$ bar atmosphere) and excellent chemical stability, which can be further improved by mixing of the ionic conductor like YSZ or GDC into the fuel electrode material [62]. Incorporating the GDC phase in the fuel electrode also improves the electrocatalytic performance of the SOFC anode [63,64]. Huang et al.[65] reported a significant decrease of electrodes R_p by mixing oxide ion-conductive electrolyte material with LST. This effect indicates insufficient ionic conductivity of LST.

B-site cations have a high impact on the electronic conductivity of SrTiO_3 -based materials. The cation's ability to attain multiple oxidation states allows electron hopping from $\text{B}^{(n-1)+}$ to B^{n+} . Therefore, B-site doping is also an effective way to improve material conductivity. Numerous elements (Mn, Zn, Ni, Cr, Ge) have been studied as a possible dopant for titanate's B-site [66–69]. In the case of $\text{LSCT}_{\text{A-}}$, Ni and Fe doping successfully increased the materials electronic conductivity [70].

The stoichiometry in perovskite and A-site deficiency significantly influence the quantity of elements on the surface. Thus, especially the B-site dopant, due to its multivalent nature, determine MIEC materials electrocatalytic properties.

It has been shown that the conductivity of LST based electrodes depends on thermal treatment. The material that has been thermally treated at high temperatures at a reducing atmosphere can have an order of magnitude higher conductance compared to materials treated at lower temperature and/or in air atmosphere [57].

LST-based materials have demonstrated excellent redox stability – less than 0.1% relative expansion at 1000°C when the gas atmosphere is switched from air to low oxygen-containing ($p_{\text{O}_2} = 10^{-18}$) atmosphere [56].

As mentioned already, one of the indicators for the chemical stability of the electrode is its suitability with the electrolyte material. Neagu and Irvine [71] tested the compatibility of YSZ with LST in the air at 1400°C and reported that no reaction takes place between these materials, which indicates titanates good compatibility with electrolyte. However, Chen et al. [72] observed solid-state diffusion of Ti from LST into $(\text{Sc}_2\text{O}_3)_{0.10}(\text{CeO}_2)_{0.01}(\text{ZrO}_2)_{0.89}$ (ScCeSZ) electrolyte material and Zr and Sc interdiffusion into LST at 1200°C in air. Based on cases mentioned above and conclusions made in literature [60] it could be stated that mobility of Sr, i.e. reactivity of LST-based material with zirconia-based electrolyte is highly sensitive on the precise cationic stoichiometry of MIEC material. Moreover, the electrochemical activity also is dependent on the exact stoichiometry of the material.

4.3.3. Surface activation by particle ex-solution

Very active surfaces can be synthesized using *ex-situ* methods like infiltration of catalyst particles [71,73,74]. However, with redox ex-solution, it is possible to get an active surface during cell operation [71]. Exsolved particles have a low tendency to merge even if they are very closely packed together (spaced by less than one particle diameter) [75]. Exsolved Ni-particles have exceptional resistance to coking when a hydrocarbon is used as a fuel for SOFC [75,76]. Another great aspect of ex-solution is that it is usually mostly reversible [77]. This means that these particles can be re-dissolved in the host lattice by oxidation and then re-exsolved upon reduction. However, this process is not fully reversible and not applicable to every system [78].

Redox ex-solution seems to be driven by phase decomposition and controlled by defects, temperature and gas atmosphere [75,79]. During the reduction, the lattice loses oxygen and gains electrons. At one point, when the defect concentration reaches a certain threshold level, B-site cation nucleation takes place. B-cation migration in perovskites is likely to occur between adjacent B-sites along a curved trajectory in the (110) planes [80]. At one point, the metallic form becomes favourable for the cation, which leads to its ex-solution.

Enrichment of surface with A-site cations hinders the exsolution of B-site cations, which is one reason why A-site deficiency is used in these materials [75,81,82]. The A and oxygen-site deficient perovskite may also be considered as B-site excess, which also explains the B-site cation ex-solution. Another important aspect that defines the surface processes is the extent of B-site cation reduction. It has been found that even with 20% A-site deficiency, exsolution does not take place if the extent of B-site reduction is under 5% [81].

4.4. Factors influencing the cell voltage

According to the Nernst equation, the SOC at open circuit conditions has a potential difference (E) between the electrodes. It is related to the SOC reaction free energy change, ΔG ,

$$\Delta G = -nFE \quad (7)$$

where n denotes the number of electrons participating in the reaction and F is Faraday constant. In this case, the Nernst potential is called the theoretical open-circuit voltage (OCV) of the SOC. It can be calculated using the following formula (if hydrogen is used as a fuel):

$$E = -\frac{\Delta G}{nF} = -\frac{\Delta G}{2F} = -\frac{\Delta G^0}{2F} - \frac{RT}{2F} \ln \left(\frac{p_{H_2O}^f}{p_{H_2}^f p_{O_2}^a} \right) = E^0 + \frac{RT}{4F} \left(\frac{p_{H_2}^f{}^2 p_{O_2}^a}{p_{H_2O}^f{}^2} \right) \quad (8)$$

where $p_{O_2}^a$ is the partial pressure of oxygen in the air electrode compartment, $p_{H_2}^f$ and $p_{H_2O}^f$ are respectively, the partial pressures of H_2 and H_2O in the fuel electrode compartment, R is the ideal gas constant, and T is the absolute temperature.

The Nernst potential is not a function of current density (i) and is constant as long as $p_{O_2}^a$, $p_{H_2}^f$, $p_{H_2O}^f$ are fixed values. However, suppose the gas flow rates in both electrode compartments are not high enough. In that case, the concentration of the reactants will change during the operation, which will lead indirectly to the change in Nernst potential [6,22,83].

A significant amount of energy is lost to heat (and entropy, depending on reaction) when converted with SOC. Unless SOEC is used at thermoneutral potential, where the heat generated in the SOC is used to activate the endothermic electrolysis reaction, in this case, the theoretical conversion efficiency is 100%. It will be slightly lower in practice due to gas leakage, heat losses, and electronic losses through the electrolyte [84].

The conversion losses result in the change of cell potential from the OCV to lower potentials, in the case of SOFC, and higher potentials in SOEC. The cell potential change due to current density through the cell is often referred to as polarization. The cell voltage dependence on current density curves is called a polarization curve (or i - V curve) [6,22,85].

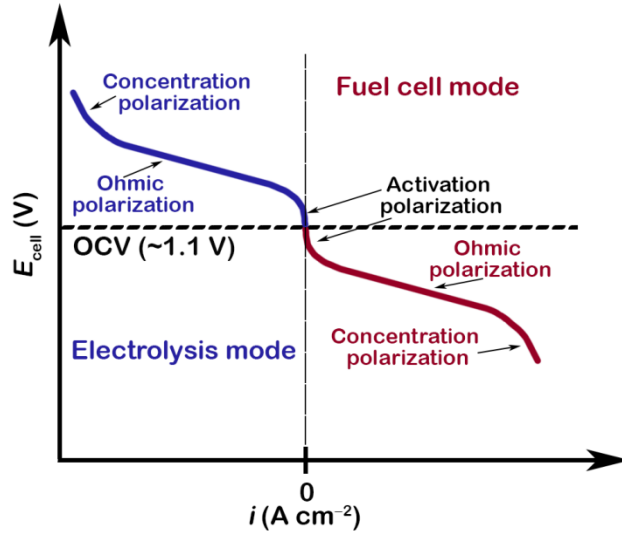


Figure 2. Typical solid oxide cell polarization curve. The blue line corresponds to electrolysis mode and the red line to fuel cell mode.

In Fig. 2, a typical polarization curve for solid oxide cells is given. The curve has three characteristic regions that have distinguishably different slopes. The contrast comes from the difference in the origin of the voltage loss. The closest region to OCV conditions (0 A) is referred to as activation polarization. The middle linear polarization region is called the ohmic polarization since the voltage drop follows Ohm's law. The highest current density region is named the concentration polarization.

Activation polarization is an unspecific term that is used for different reaction rate limitations. Usually, it is used when the limitation is in the non-linear low-current region of the polarization curve. However, it is not exactly distinguished what is at hand. The limitation's origin might be related to several processes taking place at either of the electrodes. Some of these are:

- Processes that are related to reactant molecules – adsorption at the electrode or bond breaking
- Surface diffusion of intermediates to TPB
- Transfer of ions through the electrode/electrolyte interface
- Electron transfer to molecule
- Desorption of reaction products

Concentration polarization, similarly to activation polarization is also a general term. The term “concentration polarization” is used for all kinds of physical “resistance” to the gaseous species transport on either of electrodes. During the transport of the gaseous reactants from the gas phase to the reaction site different processes like diffusion and adsorption/desorption at the electrode surface can occur [6,86,87].

Cyclic voltammetry is an excellent tool for estimating actual cell or electrode performance. The power density (P) from these curves can be calculated:

$$P = Ei \quad (9)$$

However, to identify the limiting processes in the electrode and to quantify the impact of these processes on cell performance, additional information from other methods is necessary. One of these methods could be electrochemical impedance spectroscopy (EIS).

4.5. Electrochemical impedance spectroscopy

EIS experiment involves excitation of an electrochemical cell with low alternating voltage amplitude at different frequencies and measuring the current response (Fig. 3). The experiment can also be done *vice versa* (with current excitation and voltage response). However, the measurement can only be conducted at steady-state conditions. In the case of voltage perturbation, the signal can be expressed as:

$$V(t) = V_0 \sin(\omega t), \quad (10)$$

where $V(t)$ is alternating voltage (AV) at a specific time, V_0 is AV amplitude value, ω is the angular frequency $\omega = 2\pi f$, f is the frequency of the perturbation signal.

The current response to the perturbation is also expressed as a sinusoidal wave:

$$I(t) = I_0(\omega) \sin(\omega t + \varphi(\omega)), \quad (11)$$

where $I(t)$ is the alternating current (AC) response to the alternating voltage at a specific time, I_0 is the frequency-dependent AC amplitude value, $\varphi(\omega)$ is the frequency-dependent phase shift between the voltage and current wave forms. According to Ohm's law, the overall impedance is calculated from a ratio between complex variables of voltage and current:

$$Z(\omega) = \frac{V(t)}{I(t)} = |Z(\omega)| e^{j\varphi(\omega)} = |Z(\omega)| (\cos\varphi(\omega) + j\sin\varphi(\omega)), \quad (12)$$

where $Z(\omega)$ is frequency-dependent total impedance and j is the imaginary unit. The total impedance can be separated into real ($Z(\omega)'$) and imaginary part ($jZ(\omega)''$):

$$Z(\omega) = Z(\omega)' + jZ(\omega)'' \quad (13)$$

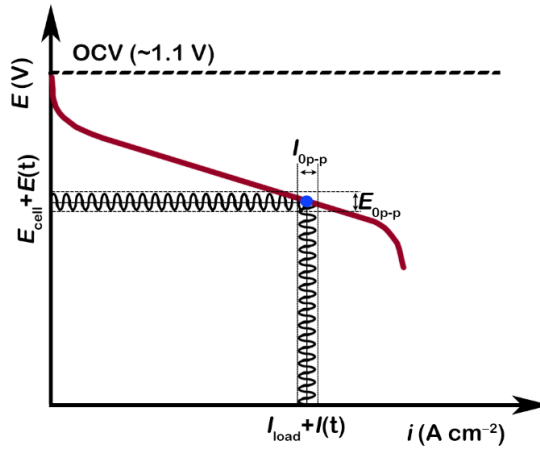


Figure 3. Schematic of impedance measurement. A sinusoidal voltage ($E(t)$) with small amplitude (peak to peak amplitude in the figure, E_{0p-p}) is applied to steady-state cell voltage (E_{cell}) as excitation, and the current response $I(t)$ with current amplitude (peak to peak amplitude in the figure, I_{0p-p}) is measured.

The measurement is usually carried out at a fixed number of defined frequencies. The real- and the imaginary part of impedance at those frequencies are plotted in a complex plane, called the Nyquist plot (Fig. 4). The first intercept at high frequencies in the SOC Nyquist plot corresponds to the high-frequency series resistance or ohmic resistance of the cell (R_s), mainly caused by the electrolyte resistance. The difference between the low and high-frequency intercept corresponds to the polarization resistance (R_p) of the cell (Fig. 4), which combines all the reaction resistances in both electrodes, including mass-transfer, charge-transfer and adsorption limitations [6,85,88,89].

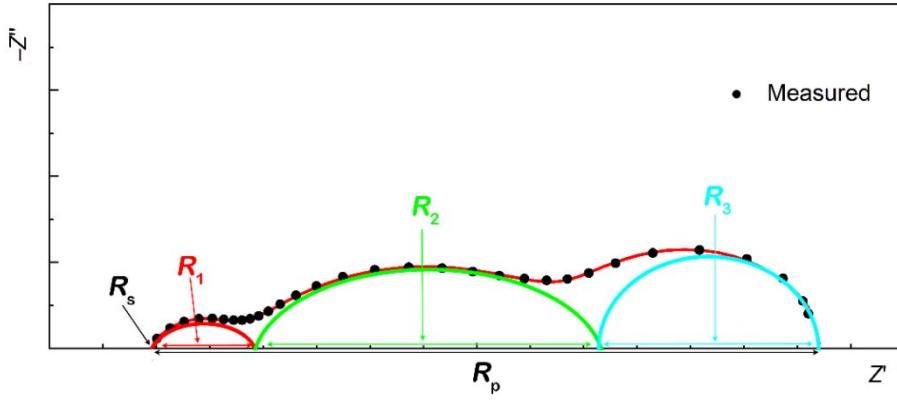


Figure 4. Experimental Nyquist plot (black dots) and the fitting result (red line) with a priori defined equivalent circuit model consisting of R_s in series with 3x -RCPE-elements.

There are two approaches to characterize only a single SOC electrode resistances with EIS. Firstly, it is possible to measure symmetric cell with identical electrodes at 0 V AV potential with small AV perturbation. The measurement gives the sum of both electrodes polarization resistance, divided by 2 to get it for the single electrode. However, this measurement cannot be conducted at *operando* conditions, i.e., no current can go through the cell. Characterization at operating conditions is possible using a 3-electrode system with a reference electrode (RE) in addition to the working electrode (WE) and counter electrode (CE). In this case, the small AV signal is superimposed on a DV polarization. However, according to the literature, the thin film solid electrolyte configuration is not ideal for accurate impedance studies. Many errors arise with the misplacement of electrodes. Generally, to minimize errors, exact alignment of WE and CE is necessary, and the distance between RE and WE should be at least 2-3 times the electrolyte thicknesses [90–93].

4.5.1. Equivalent circuit fitting

Separating the limiting processes using EIS relies on the fact that various limiting processes have different time constants. To identify the limiting processes in the system and evaluate the magnitude of the different physical processes and time constants mentioned in chapter 4.4. an equivalent circuit consisting of RLC elements (resistors, inductors, capacitors) should be developed. The following (Table 1) parameters govern the response of an electrical circuit consisting of a single RLC element:

Table 1: Properties of different equivalent circuit elements (resistor, inductor and capacitor). $|Z|$ corresponds to the magnitude of impedance, Z' to the real part of impedance, Z'' to the imaginary part and φ to phase shift between the voltage and current waveforms.

	$ Z $	Z'	Z''	φ
Resistor	R	R	0	0
Inductor	ωL	0	$j\omega L$	90°
Capacitor	$1/\omega C$	0	$-j/\omega C$	-90°

The fundamental element to describe electrochemical processes resistive-capacitive behaviour is the RC element, a parallel circuit of an ohmic resistor, and a capacitor. The impedance of the RC element (eq. 14) is called Z_{arc} since it corresponds to an arc in the Nyquist plot and a specific limiting process in the system.

$$Z_{arc} = \frac{R}{1+j\omega\tau_{RC}}, \quad (14)$$

Where τ_{RC} is the time constant for the specific limitation ($\tau_{RC} = RC$).

However, since the SOC electrode has complex microstructure and 3d porosity, its microstructure differs from 2d ideal capacitor plate. As a consequence, the time constants (resistive and capacitive behaviour) for different processes might vary over different regions on the electrode. So limiting processes instead of having a concrete relaxation time, usually are characterized by a distribution of relaxation times around maximum. In order to describe this kind of behaviour, constant phase element (CPE) is usually used. The mathematical representation for it is given in eq. 15. A Nyquist plot fitted with R in series with 3x - RCPE- element is given in Fig. 4 [6,89,94–96].

$$Z_{CPE} = A^{-1}(j\omega)^{-\alpha_{CPE}}, \quad (15)$$

where A is the CPE coefficient and α_{CPE} is the fractional exponent. If α_{CPE} is 1, then CPE is equal to capacitor. However, if α_{CPE} is 0.5, then the 45° line is

produced on the complex plane plot. If CPE is put to in a parallel circuit with a resistor, then depressed semi-circle is formed [94].

The Nyquist plot is fitted, i.e., unknown values of different equivalent circuit elements are usually evaluated, using Complex Nonlinear Least Squares (CNLS) fit. The quality of modelling is estimated using the chi-square function (χ^2), and the weighted sum of squares (Δ^2) is used to get relative error parameters [97].

Unfortunately, very rarely, EIS can be used as a “standalone” method to identify the limiting processes in the SOC. More information from other methods (preferably *operando* methods) is needed to construct or validate the equivalent circuit used for fitting.

4.6. X-ray diffraction

SOC electrodes and electrolyte are polycrystalline. The electrochemical activity and stability of these materials are dependent on the crystallographic properties and chemical composition of different phases in the material. X-ray diffractometry (XRD) can give averaged information about crystallographic bulk properties. Distinguish the arrangement of atoms, identify them and quantify their amount in the unit cell. It is also possible to evaluate strain, domain sizes for different phases and identify and quantify defects in the lattice. However, deconvolute all this information, high-quality data is necessary [98–100].

The maxima in the diffraction pattern resulting from constructive interference between X-ray waves (usually monochromatic) that have elastically scattered from different lattice planes. The condition for constructive interference at a certain diffraction angle is given in the Bragg equation [101,102]:

$$n\lambda = 2d \sin \theta, \quad (15)$$

where n is an integer number, λ is X-ray wavelength, d is the distance between lattice planes and θ is diffraction angle.

The amount of independent lattice plane sets (d -spacings) that one crystal structure can have is defined by its lattice parameters, which describe the unit cell’s size and shape. The number of unit cell parameters depends on the phase’s crystal symmetry varying from 1 (in the highest crystal symmetry *cubic*) to 6 (lowest crystal symmetry, *triclinic*). Therefore, if we know the lattice’s crystal symmetry and Bragg peak positions (d -spacing), it is possible to calculate lattice parameters [103,104].

The unit cell contents and their positions are coded in the relative integral intensities (area) of the diffraction maxima for given crystalline phase. The integral intensity of a Bragg peak with plane indices hkl (I_{hkl}) corresponds to:

$$I_{hkl} = CM|F_{hkl}|^2, \quad (16)$$

where C corresponds to different corrections with the most significant perhaps being: Lorentz and polarization corrections, which are dependent on the precise geometry; Debye-Waller factor, which is due to thermal vibration of the crystal; absorption correction, which is related to X-ray absorption in the material. M corresponds to the multiplicity factor, which takes into account that some lattice planes have other family planes with the same spacing. For example, (100) plane in cubic symmetry has five other family planes ((010), (001), ($\bar{1}$ 00), (0 $\bar{1}$ 0), (00 $\bar{1}$)) that contribute to the same Bragg peak. F_{hkl} is the structure factor, which in the case of XRD corresponds to the Fourier transform of the electron density [99,103,105].

Theoretically, perfect diffraction from an ideal crystal should result in indefinitely sharp reflection. Unfortunately, neither the experimental setup nor the sample is ever perfect. This leads to peak profile broadening. Instrumental function describes the instrumental broadening at a certain diffraction angle. Sample related contributions take into account imperfections in the crystal (crystal size, defects and stacking faults).

Scherrer [106] gave a basic empiric definition for the “apparent” domain size, which can be calculated from a single Bragg peak:

$$p = \frac{K\lambda}{\beta \cos \theta'} \quad (17)$$

where p is true crystallite size, K is Scherrer constant (shape factor), β is an integral breadth of diffraction peak (which must be corrected for instrumental broadening). However, the full width half maximum (FWHM) was used initially and sometimes still is used instead of β .

However, since it is a single peak analysis, it misses any anisotropy effects. The other problem lies with a Scherrer constant, which depends on the shape of the crystal. In practice, crystallites usually are irregular in shape, but on average, they may often be regarded as having a regular external form. Langford and Wilson [107] have defined the shape factor for four different crystallite shapes for all the lattice planes depending on the crystal symmetry (cubic, tetrahedral and octahedral). Another problem with the Scherrer equation is that it doesn't take strain broadening into account. Although the Scherrer equation is very popular for crystallite size determination, it should be used cautiously [107,108].

Another widely used method is based on the assumption that both size and strain (ϵ) broadening is Lorentzian, which plot integral breadths of all diffraction maxima against the diffraction angle. These methods are based on the Williamson-Hall equation [109]. One of these modified variants is the uniform deformation model [110,111]:

$$\beta \cos \theta = \frac{k\lambda}{p} + 4\epsilon \sin \theta. \quad (18)$$

However, this method only works if the peaks are not overlapping. Moreover, it does not work if there is an anisotropic line broadening [108].

The Double-Voigt approach is one of the modern methods for XRD line broadening analysis, where both size and strain are considered Voigt functions, which is a convolution of both Gaussian and Lorentzian. This method works in part of the whole pattern fitting where all the different contributions (including instrumental) to the maxima are fitted. Thus, the overlapping of peaks is less of an issue. The differentiation of strain and crystallite size comes like in the Williamson-Hall method from the angular dependence. However, this method's drawback is that a good fit of the whole diffraction pattern is necessary to get any meaningful results [108,112].

5. EXPERIMENTAL

5.1. Preparation of single cells

Electrolyte supported single cells were all prepared under well-controlled conditions. Either commercial 250 mm thick $(\text{Sc}_2\text{O}_3)_{0.10}(\text{CeO}_2)_{0.01}(\text{ZrO}_2)_{0.89}$ (ScCeSZ) (Kerafol) membranes or 220 μm thick membrane with the same chemical composition prepared in-house from dense electrolyte films were used.

Electrolyte paste for dense electrolyte layer was made of $(\text{Sc}_2\text{O}_3)_{0.10}(\text{CeO}_2)_{0.01}(\text{ZrO}_2)_{0.89}$ (ScCeSZ) powder (Sc10Ce1SZ-TC, Fuel cell materials) mixed with solvents (ethanol and xylenes, both from Sigma Aldrich) and dispersant (Menhaden fish oil, Sigma Aldrich) in a weight ratio 30:23:1, respectively, and ball-milled for 24 h. The binder (polyvinylbutyral B-98, Sigma-Aldrich) was added to the mixture in a weight ratio 2:27 and homogenized for additional 24 h before adding the plasticizers (polyethylene glycol with an average molecular weight of 400 g/mol, Aldrich; benzyl butyl phthalate, Merck) in a weight ratio 3:56 and ball-milled another 24 h. The slurry's de-gasification was achieved by the very slow rotation of the paste for a minimum 24 h. The slurry was cast using AFA I Automatic Thick Film Coater (MTI Corporation) with a speed of 40 mm/s. The tapes used to form porous electrolyte scaffolds were prepared similarly except that different ethanol-to-xylene ratio (2.5:10) were used to accommodate the pore former's addition (graphite with particle size distribution 2–15 μm , TIMCAL).

ScCeSZ wafers were fabricated by laminating together either four green tapes (porous-dense-dense-dense) if the fuel electrode was impregnated into porous electrolyte matrix or three green tapes (dense-dense-dense) if the fuel electrode was added either by screen printing or pulsed laser deposition (PLD) on the electrolyte. Laminating was done using isostatic compression (isostatic laminating system ILS 46, Keko Equipment) and followed by sintering at 1400 $^{\circ}\text{C}$ for five hours. The dense electrolyte thickness was 220 μm , and the geometric surface area of the porous electrode, if used, was 0.87 cm^2 .

In all experiments, the oxygen electrode was the same and was made of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) paste, as described in ref [113]. In order to avoid the formation of a poorly conductive SrZrO_3 phase, the $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (Fuel cell materials) chemical barrier layer was deposited between the cathode and the electrolyte using a screen-printing method. The thickness of the electrode was always 40 μm . However, the active geometric surface area was in the first experiments (when Ni-GDC was used as a fuel electrode) 0.28 cm^2 due to the spatial limitations of the initial *operando* XRD-cell. In all the other experiments (when a full ceramic fuel electrode was used), 0.87 cm^2 was the active geometric surface area.

Three different fuel electrode groups were studied in this thesis. Firstly, the Ni-GDC electrode was studied as a model system to evaluate the developed *operando* XRD method's capabilities. Secondly, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSCMN)

with also two different microstructures was studied. Finally, $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ (LSCNT-x) at five different Ni concentrations ($x = 0, 0.02, 0.05, 0.1, 0.2$) were studied.

An 8 μm thick Ni-GDC fuel electrode porous anode with a 0.5 cm^2 geometric surface area was prepared using the screen-printing method. The screen-printing paste was from Fuel Cell Materials (60% NiO, 40% $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$), which was diluted in isopropanol, so the concentration of the paste would decrease five times to get a thin enough electrode, so the X-rays could penetrate through the whole electrode. The calculated penetration depth for 99% of X-rays at 2θ value corresponding to the GDC (220) maximum was 8.5 μm . The electrode was sintered at 1350 $^{\circ}\text{C}$.

A nonporous LSCMN electrode was deposited on the ScCeSZ electrolyte with a pulsed laser deposition (PLD) method. The LSCMN pellet was used as an ablation target, and a KrF excimer laser (COMPexPro 205, Coherent; wavelength 248 nm; pulse width 25 ns) was used for deposition. The target was ablated by using a laser pulse energy density of 3.3 J/cm^2 in the oxygen background of 5×10^{-2} mbar. Substrates were kept at 700 $^{\circ}\text{C}$. Other typical process parameters are as follows: laser pulse repetition rate 10 Hz, the total number of laser pulses applied was 72000, and the distance between the substrate and the target was 75 mm.

The porous LSCMN fuel electrode was made by impregnating the porous ScCeSZ scaffold with aqueous solutions of corresponding salts with stoichiometric proportions. The raw solution for preparation of the fuel electrode consisted of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Alfa Aesar), $\text{Sr}(\text{NO}_3)_2$ (99.9%, Alfa Aesar), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%, Alfa Aesar), $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99.9%, Alfa Aesar) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.999%, Sigma-Aldrich). Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the exact stoichiometry of raw solutions (8800 QQQ ICP-MS, Agilent). The citric acid in a molar 1:1 ratio (metal cations) was used as a complexing agent for LSCMN solution in order to assist the formation of the perovskite phase at lower synthesis temperatures. Each impregnation step was followed by a 0.5 h heat treatment at 450 $^{\circ}\text{C}$ to decompose the selected and deposited nitrates. This procedure was repeated until the desired mass loadings of LSCMN (50 mass%) was achieved. The synthesized electrodes exact stoichiometry was $\text{La}_{0.75(\pm 0.015)}\text{Sr}_{0.25(\pm 0.005)}\text{Cr}_{0.50(\pm 0.017)}\text{Mn}_{0.30(\pm 0.008)}\text{Ni}_{0.20(\pm 0.004)}\text{O}_{3-\delta}$. The mass percentage of a mixed ionic electron conductor (MIEC) was calculated relative by dividing MIEC material mass with a total weight of porous scaffold plus the MIEC material mass itself. As a final step, the cell was calcined at 1000 $^{\circ}\text{C}$ for five hours.

The LSCNT-x fuel electrodes were made using the screen-printing method. The electrode powders were prepared by using the glycine-nitrate combustion synthesis method. Nitrate solution was prepared using $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Alfa Aesar), $\text{Sr}(\text{NO}_3)_2$ (99.9%, Alfa Aesar), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.999%, Sigma-Aldrich), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.9%, Alfa Aesar) and $\text{C}_6\text{H}_{18}\text{N}_2\text{O}_8\text{Ti}$ 50% solution in water (Sigma-Aldrich), as precursor materials and glycine (99%, Sigma Aldrich) as reducing agent was applied. The mole ratio of the sum of metal

cations to glycine was 1:1.5. This time, the exact concentrations of the precursor solutions were determined using thermogravimetric analysis (STA 449 F3 Jupiter, Netzsch) for each metal cation raw solution, except Ca^{2+} solution, which was analyzed using ICP-MS (8800 Triple Quadrupole ICP-MS, Agilent). The reason for not using ICP-MS for all of the solutions was better reproducibility of TGA measurements and systematic errors in evaluating Ti(IV) concentration with ICP-MS. The synthesized powders were calcined at 900 °C for 20 h. The exact stoichiometry of the synthesized powders (Table 2) was confirmed with X-ray fluorescence spectrometry (XRF) (Rigaku ZSX Primus II) using glass bead standards made in-house with borate fusion.

Table 2 Expected and experimentally obtained (based on XRF analysis) cationic stoichiometries in $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ powders.

Stoichiometry of interest	Abbreviation	La	Sr	Ca	Ti	Ni
$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{TiO}_{3-\delta}$	LSCT	0.25	0.26	0.39	0.99	0
$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.98}\text{Ni}_{0.02}\text{O}_{3-\delta}$	LSCNT-2	0.25	0.26	0.39	0.97	0.02
$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$	LSCNT-5	0.25	0.26	0.39	0.94	0.05
$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$	LSCNT-10	0.25	0.25	0.40	0.91	0.10
$\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$	LSCNT-20	0.25	0.25	0.40	0.79	0.20

To increase the ionic conductivity of the electrode, GDC (fuel cell materials) powder was mixed with LSCNT-x (1:1 weight ratio). Additives used to make screen-printing raw-paste from the powder were α -terpineol (SAFC), which was used as a solvent, Solsperse 3000 (Lubrizol), which was used as a dispersant, polyethylene glycol (Sigma Aldrich), which was used as a binder and polyvinyl butyral (Sigma Aldrich) as a plasticizer.

5.2. Electrochemical measurements

Solartron 1260 frequency response analyzer and 1287 potentiostat were used in combination with Probostat[™] (NorECS ceramics) measurement cell for all of the electrochemical measurements. For *operando* XRD measurements, Gamry interface 1000A was used in combination with a cell developed in-house explicitly for *operando* experiments. The single cells were always studied at gas overflow conditions, where both anode and the cathode chamber gas flows were controlled by Bronkhorst EL-FLOW SELECT F-201CV mass flow controllers.

The two-electrode cell configuration was used only for electrochemical measurements of porous impregnated LSCMN electrodes. A three-electrode setup was used to control the studied electrode's potential with all the other measured electrodes. The Pt/porous Pt in O₂ (Pt/Pt/O₂) was used as the RE. The reference electrode was placed onto the same side and approximately 1 mm from the CE for the experiments with Ni-GDC and LSCMN electrodes. The RE electrode in the case of the LSCNT-x electrode was placed onto the same side and approximately 1 mm from the WE to avoid gas conversion impedance.

In all the electrochemical experiments, synthetic air was used as an oxidant. Humidified hydrogen was used as a fuel in all the SOFC mode experiments; however, with different concentrations, mixed with inert gas (either Ar, N₂ or He). "Humidified" in this thesis context means that the used fuel mixture was lead through a gas bubbler containing MilliQ⁺ water at 24 °C (3% H₂O uptake).

Impedance spectra for the LSCMN electrode were measured with the AV amplitude of 5 mV. The frequency region from 0.2 Hz to 1,000,000 Hz was recorded under specific cell potentials (OCV, -0.8 V in fuel cell mode and -1.5 V in steam electrolysis mode). Current collectors were made from Au (lot no. 1120912, SPI supplies), which is catalytically relatively inactive the stripe shape current collectors were made using a stencil printing method. The stability tests were conducted in two different gas compositions (humidified H₂ in fuel cell mode, and 30% H₂O, 70% H₂ in electrolysis mode). The electrochemical measurement procedure is given in Fig. 5. The single-cell's electrochemical stability was tested at -1.5 V in electrolysis mode and at -0.8 V in fuel cell mode at 850 °C. After every 24–48 h, the temperature dependence of polarization resistance (R_p) and series resistance (R_s) was measured in order to calculate the activation energies for their limiting processes. After the initial electrochemical characterization, the impact of a redox cycle on the fuel electrode characteristics was studied. For the redox cycle, the gas atmosphere in the fuel electrode compartment was changed slowly from the fuel mixture to the synthetic air atmosphere, where it was kept for 10 h. After reoxidation, the fuel electrode was gradually reduced again, and its effect on cell performance and stability was studied.

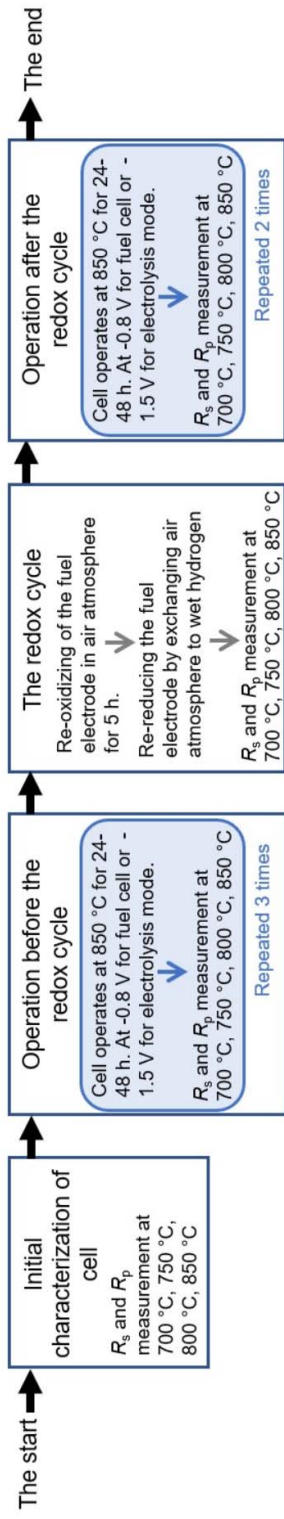


Figure 5. The sequence of different measurement steps during LSCMN stability tests.

Impedance spectra for LSCNT-x electrodes were recorded under specific electrode potentials (OCV and -0.9 V) with the AV amplitude of 10 mV and the frequency region from 0.01 Hz to 600,000 Hz. Cyclic voltammograms were recorded using a scan rate of 5 mV s^{-1} . Two different hydrogen concentrations were studied – humidified H_2 ; humidified 50% H_2 , 50% Ar.

5.3. Physical characterization of the materials

Bruker-AXS D8 X-ray diffractometer with a Cu $\text{K}\alpha$ radiation source (40 kV, 40 mA, a Goebel mirror, 2.5° Soller slits, and LynxEye 1D detector) was used for all the XRD measurements, including *in situ* and *operando* measurements, excluding Grazing Incidence XRD (GI-XRD) measurements. The lattice parameters were calculated using Topas software (version 4 and 6), and the XRD full profile has been fitted using Fundamental Parameters peak type [114], using known Au or corundum lattice parameters as a reference. The full profile fit was considered sufficiently good if the residual (weighted pattern) values were lower than 5%.

The PLD LSCMN electrodes GI-XRD measurement was performed on diffractometer SmartLabTM (Rigaku) using a Cu rotating anode working at 45 kV and 18 mA, 0D scintillation detector, and parallel beam optical geometry with 0.115° Soller slit analyzer. The diffraction pattern was measured between diffraction angles of 19 and 70° with a step size of 0.02° .

The microstructure of the electrodes was characterized with a scanning electron microscope either high-resolution SEM Zeiss Merlin or Zeiss EVO MA 15.

Time-of-flight secondary ion mass spectrometer (TOF-SIMS) (PHI TRIFT V nanoTOF instrument) was used to visualize the microstructural and chemical changes in LSCNT-x electrode taking place during sintering and cell operation.

Photoelectron spectra of LSCNT-x samples were measured by the hemispherical analyzer (Scienta SES100) at pass energy 200 eV and using Al- $\text{K}\alpha$ radiation, with an overall resolution of approximately 0.8 eV. Curve fitting analysis of all photoelectron spectra was done using the SPANCF package [115,116].

5.3.1. *operando* and *in situ* XRD measurements

The Anton Paar HTK 1200N high-temperature (HT) XRD chamber was modified to a dual-chamber setup to allow different gas atmospheres for both electrodes and internal electrical contacts inside the chamber. The anode and cathode gas compartments were both inside HT-cell and separated from the room atmosphere and each other. The HT-chamber's gas-tightness was achieved with rubber o-rings in the low-temperature part of the high-temperature chamber. The cathode and anode compartment was separated from each other with a glass

seal from Scotch. The p_{O_2} in the anode compartment was controlled by monitoring OCV (the p_{O_2} in the cathode compartment was known). The schematic drawing of the measurement cell is given in Fig. 6.

Operando XRD Ni-GDC measurements were conducted in 2 different gas atmosphere (1% H_2 , 99% Ar and 5% H_2 , 95% Ar). Impedance spectra were recorded at fixed electrode potentials and with AV amplitude of 10 mV, with a frequency range from 0.2 to 100,000 Hz.

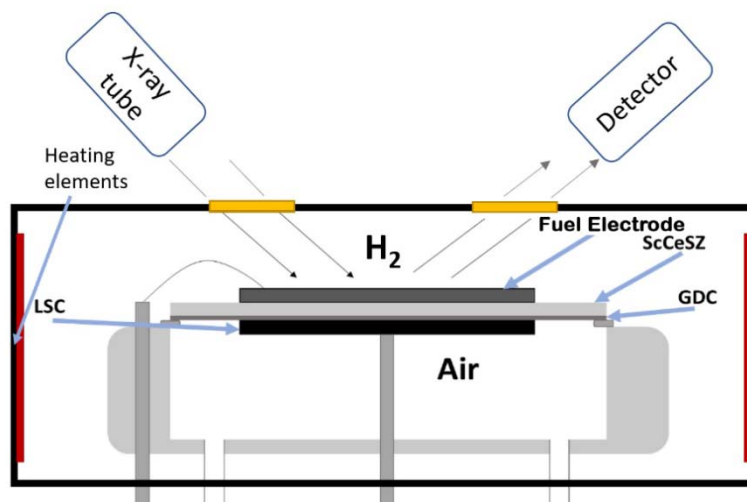


Figure 6. Schematic drawing of used *operando* XRD cell, where the high-temperature chamber has two gas-tight compartments for the fuel mixture (noted as H_2 in the figure) and synthetic air (noted as air in the figure), respectively.

With 5 mV AV amplitude and frequency of 0.2 Hz to 10,000 Hz, impedance spectra were recorded in *operando* XRD LSCMN electrode at specific cell potentials (-0.8 V and OCV). In the hydrogen gas compartment, two different humidified gas compositions were used as fuel (5% H_2 , 95% He and 10% H_2 , 90% He). The experiments were conducted in the temperature range from 700 to 850 °C. After the initial *operando* characterization of electrochemical- and crystallographic properties, the impact of a redox cycle on the single-cell characteristics has been studied. For the redox cycle, the anode compartment gas atmosphere was changed to 100% He at first, then to 2% O_2 in He and then to 100% O_2 . After full oxidation of hydrogen electrode, the electrode was reduced again – at first, 100% He was introduced and then 5% H_2 in He. After the electrochemical and crystallographic monitoring of the redox cycle at *operando* conditions, the single-cell was characterized again at the same conditions as prior to the redox cycle.

In situ XRD characterization of LSCNT-x powder was carried out in 3 different gas compositions (humidified 10% H₂ in N₂; humidified 5% H₂ in N₂; air). The measurements were conducted at four different temperatures (700 °C, 750 °C, 800 °C, 850 °C). Corundum was used as a reference for *in situ* XRD characterization at high temperature.

6. RESULTS AND DISCUSSION

The discussion section of this thesis is divided into three different parts, based on the chemical composition of the material studied. The first part focused on the *operando* XRD study of the Ni-GDC model system to assess the developed method's capabilities for future MIEC material characterization. The second focus was to characterize the electrodes' different components' crystal lattice during cell operation. The second and third part of this thesis focused on studying two electrodes from promising perovskite families to be used as a SOC fuel electrode – doped LaCrO_3 and SrTiO_3 . However, during our early experiments [117], it became evident that LSCM with our used cell configuration had serious degradation problems during the initial electrode stabilization period. So the second part of this thesis focused on understanding the reasons underlying the Ni-doped LSCM materials instability using $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ as a model system. The third part involved a detailed study of titanate-based ($\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{TiO}_{3-\delta}$) MIEC material with Ni-doping and assessing its influence on the electrochemical performance, crystallographic parameters and stability.

6.1. Ni-GDC model system *operando* XRD measurements data

Before Ni-cermets can be used as SOC electrodes at high temperatures, the NiO needs to be reduced to Ni. Thus, the *operando* experiment was started with Ni-GDC characterization during the reduction process, initiated by reducing gas atmosphere (Ar with 1% H_2 addition) to the electrode's chamber. In Fig. 7, simultaneous change of electrode's electrochemical performance and NiO reaction to Ni overtime was visualized by plotting electrode's polarization resistance R_p , relative areas of Ni (111) reflections ($2\theta = 44.0$ deg.) and NiO (200) reflections ($2\theta = 42.8$ deg.) vs time. Relative areas, which were obtained by dividing the area of Bragg peak (either NiO(200) or Ni(111)) at a certain time with the maximal area of the same reflection. Maximal areas for NiO (200) and Ni (111) were obtained from XRD patterns before and after the reduction step, respectively. As could be seen from Fig. 7, the electrode's R_p initially increased. However, suddenly after 28 minutes, before Ni(111) was even visible in the diffractograms, it had decreased quickly to a certain constant level. The initial increase of R_p could likely be explained by the formation of Ni on the NiO grain surface. It has been reported that small amounts of Ni (approx. 1%) in NiO leads to a significant (approx. 40%) decrease of oxide ion conductivity of NiO [118].

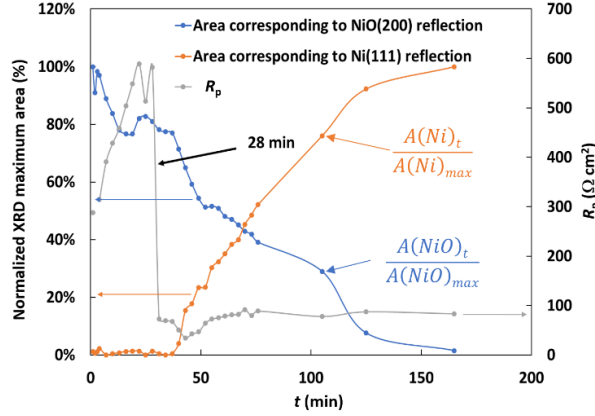


Figure 7. Change of R_p and relative Bragg peaks areas of NiO(200) and Ni(111) planes during the reduction of porous Ni-GDC electrode at 650 °C in Ar with 1% H₂. $A(\text{Ni})_t$ and $A(\text{NiO})_t$ are areas corresponding to Ni(111) and NiO(200) Bragg peak correspondingly at a specific time during reduction, $A(\text{Ni})_{\text{max}}$ and $A(\text{NiO})_{\text{max}}$ are the maximum areas of Ni(111) and NiO(200) peak correspondingly.

The first signal from metallic Ni in the XRD pattern could be seen 3 minutes after R_p 's drastic decrease. By this time, the area of NiO (200) reflection was decreased by approximately 20%, which was caused by the reduction of NiO to Ni. At the time of the drastic decrease of the R_p , approximately 20% of NiO was reduced, which is sufficient for the formation of the conductive Ni network into the electrode. The invisibility of Ni-reflection up to this point was most likely caused by too small crystallite sizes of the Ni particles and their low concentration. From Fig. 7, it could also be seen that the R_p value remained at a constant level after 60 mins of reduction. However, it took about 160 minutes to reduce the NiO entirely, which means that the R_p value at OCV conditions was within a very wide range, almost independent of the NiO/Ni ratio in Ni-cermet anode (same R_p values have been measured between 58. and 125. minute). The effect was likely caused by a slow reduction of Ni/NiO in the grain interior after 60 mins, which only slightly affects the TPB length.

The fastest Ni generation region in Fig. 7 started around 35 minutes after the start of the reaction. Simultaneously, there was a significant decrease in R_p before it stabilizes at ~60 minutes. There are two possible reasons for this kind of behaviour. Firstly, since the reduction of NiO to Ni is exothermic, it might locally increase the temperature leading to a lower fuel electrode R_p value. Secondly, the surface area and the number of active sites of just synthesized Ni might be very high, leading to a decrease of R_p . However, as mentioned in section 4.2, Ni-particles tend to coarsen to reduce their surface energy, leading to a decrease in the number of active sites and the increase of R_p . At one point (60 minutes), when the reaction rate slows down, the R_p stabilizes to some level, corresponding to a more stable surface area.

The dependence of lattice parameters of Ni-GDC phases was monitored as a function of temperature, gas composition and electrode polarization. The influence of the gas atmosphere and electrode polarization on the position (2θ value) of Ni(111) and GDC(220) peaks is visualized in Fig. 8.

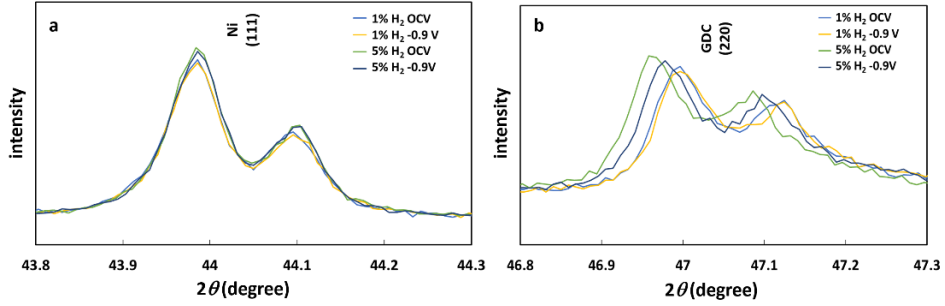
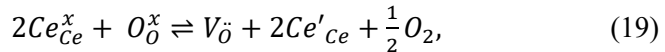


Figure 8. Ni(111) (a) and GDC (220) (b) reflections at 650 °C studied in different gas atmospheres (1% H₂ and 5% H₂ in Ar) and electrode potentials measured vs reference electrode (specified in the drawing).

Intensities of Ni(111), as well as GDC(220) reflections, were very slightly higher in the 5% H₂ gas atmosphere compared to the atmosphere with only 1% of H₂ (Fig. 8). This phenomenon was caused by higher X-ray transparency of gas mixture with higher H₂ concentration.

A very slight (but systematic) shift of Ni(111) reflection to higher 2θ values was observed when H₂ concentration increased in the electrode chamber (Fig. 8a). This very slight decrease (0.0003 ± 0.0002 Å) of the Ni lattice parameter occurs simultaneously with the shift of GDC reflections toward lower 2θ values. Most likely, the increase of GDC unit cell (lattice expansion lead to lower 2θ values) volume (Fig. 8b) develops some stress on the Ni grains. The expansion of the GDC unit cell could be explained by a partial reduction of Ce⁴⁺ to Ce³⁺ (Eq. 19). This process was accompanied by an increase of n-type electronic conductivity and release of molecular oxygen from the GDC lattice (Eq. 19) [119,120].



where Ce_{Ce}^x and O_O^x are Ce and O on their lattice site, with a neutral charge. $V_O^{\bullet\bullet}$ is oxide ion vacancy with a double positive charge. Ce'_{Ce} is a Ce-lattice site with Ce³⁺ ion and single negative charge.

The electrode polarization was accompanied by the oxide ion flux through the membrane (from the counter electrode to the working electrode), which caused a shift in the position of GDC maximum to higher 2θ values (decrease of

the unit cell). This phenomenon could be explained by the increase of p_{O_2} in the porous electrode. At OCV conditions, there was no oxide ion flux through the electrolyte, while at working conditions, there was. Thus, at operating conditions (at -0.9 V), Ce^{3+} will be partially oxidized back to Ce^{4+} , and the amount of oxide ion vacancies in GDC will decrease. This lead to a change (decrease) in the GDC lattice parameter.

The most significant polarization-induced GDC lattice parameter change was observed in the gas mixture with 5% of H_2 and 95 % of Ar (the highest H_2 concentration measured in this experiment). This was not surprising since higher fuel concentration leads to higher current densities, i.e., higher oxide ion flux through the membrane. The change of lattice parameter was not the same through the whole electrode. Most likely, in the electrode region that was close to the electrolyte, the greatest reoxidation takes place since there was also the highest current density, thus, also the highest p_{O_2} and the lowest p_{H_2} .

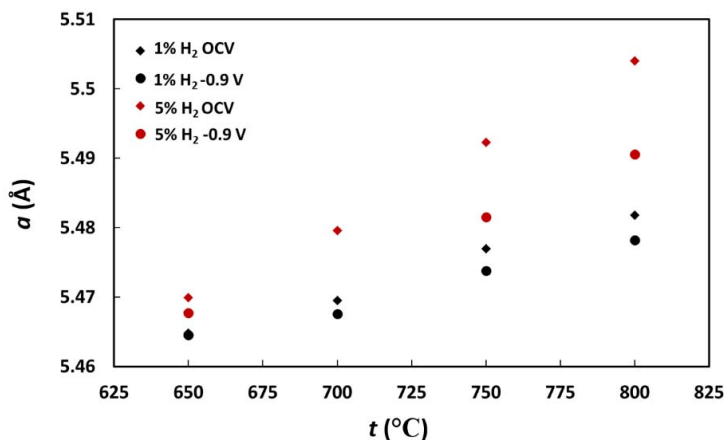


Figure 9. Dependence of GDC lattice parameter on temperature and electrode potentials measured vs reference electrode noted in the figure.

In Fig. 9, the lattice parameter of GDC is presented as a function of temperature, gas composition, and electrode potential. In addition to the effects discussed above, it could be seen that the lattice parameter increases with temperature, which is in good agreement with previous results. Thus, also, the effect of electrode potential change was higher at elevated temperatures.

Generally, high-temperature *operando* SOC XRD is an excellent tool for evaluating lattice parameter changes at SOC working conditions and in different gas atmospheres. However, to fit lattice parameters absolute values, a stable internal (mixed into electrode) reference with precisely known lattice parameters at measuring temperatures should be used. It is also quite straightforward to evaluate changes in the quantities of different phases, although it is not a very

precise method. Unfortunately, the whole diffraction profile fit with Rietveld refinement was not good enough to precisely estimate changes in the atomic occupancy and atomic positions in the unit cell. Moreover, the fit was not good enough to even evaluate stress values with the double Voigt method. However, all of this might be possible with brighter and higher resolution light sources (synchrotron).

6.2. Stability of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ electrodes

The second focus of this thesis was on understanding the reasons for $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSCMN) electrode instability during electrodes' initial stabilization period.

In Fig. 10a, the diffraction pattern of a pure phase of LSCMN with the phases corresponding to the ScCeSZ electrolyte scaffold and Au- contacts were presented. Before the electrochemical experiment, the fuel electrode structure was visualized using the SEM technique in Fig. 10b, where spherical LSCMN particles have been distinguished on top of the ScCeSZ electrolyte scaffold. No inhomogeneities in the microstructure of the electrode could be determined from SEM images in the whole electrode under study.

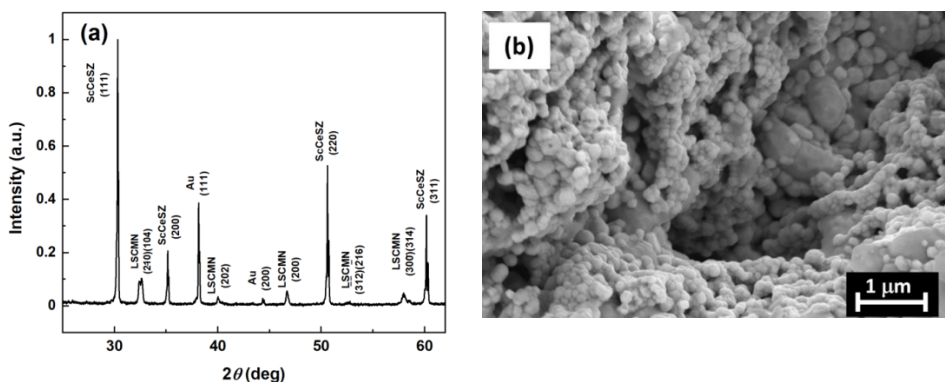


Figure 10. The diffractogram (a) of the impregnated LSCMN fuel electrode measured in air at room temperature. Reflections are labelled in the figure by the corresponding phase (ScCeSZ, LSCMN or Au) and the lattice plane indices. SEM image (b) of the cross-section of the LSCMN fuel electrode before electrochemical tests.

The degradation of material in electrolysis- and fuel cell mode has been evaluated in separate experiments to exclude the effect of electrode history on the degradation studies. Degradation of the LSCMN electrode was observed (an increase of R_s and R_p). The time-series data given in Fig. 11 is not continuous because the stability tests were stopped after every 24–48 h to measure the

electrochemical impedance at different temperatures (Fig. 5). From the data collected using impedance spectroscopy, the activation energies were calculated, and, eventually, the change of the activation energy during the whole degradation test was seen. Relatively rapid and severe degradation of the LSCMN electrode was observed in both fuel cell and electrolysis mode.

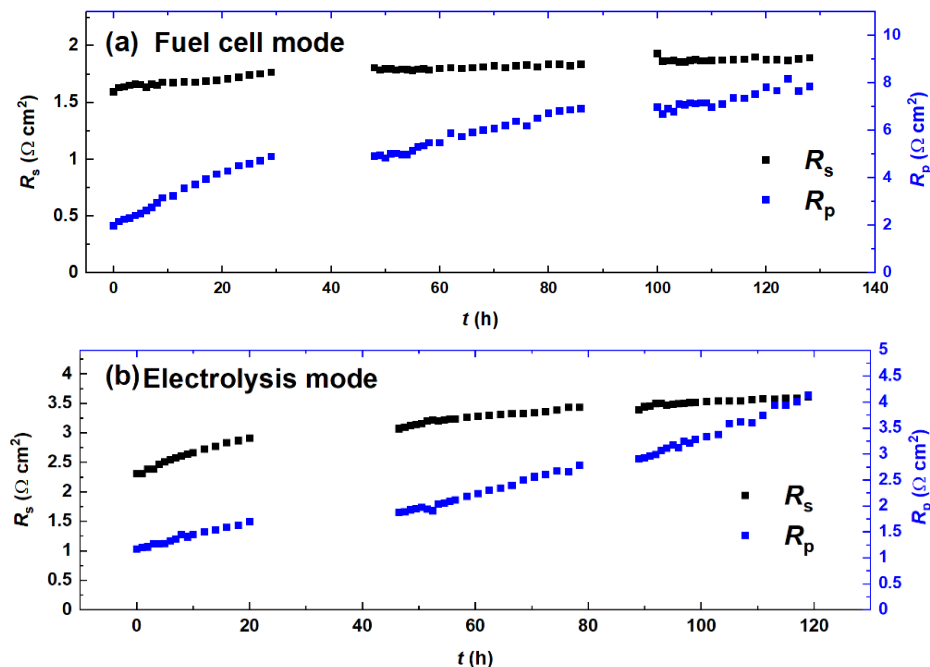


Figure 11. Dependence of R_s and R_p on time for infiltrated LSCMN electrode at 850 °C (a) in fuel cell mode (−0.8 V, 97% H₂/ 3% H₂O gas atmosphere) and (b) in electrolysis mode (−1.5 V, 70% H₂/ 30% H₂O gas atmosphere).

During the first 100 h of operation of the cell in the fuel cell mode (Fig. 11a), R_s of the cell increased 13.5% and R_p about 255%. The initial value of R_s degradation speed was approximately $0.006 \Omega \text{ cm}^2 \text{ h}^{-1}$, but the degradation rate reached a plateau by the end of the experiment. R_p 's degradation speed was more stable with a tendency to decrease in time – the initial value of R_p degradation rate was $0.1 \Omega \text{ cm}^2 \text{ h}^{-1}$, and the final value at the end of the 130 h experiment was $0.035 \Omega \text{ cm}^2 \text{ h}^{-1}$.

Similarly to the data collected in fuel cell mode, severe degradation can be seen in the electrolysis mode (Fig. 11b). The initial rate of R_s ' degradation was approximately $0.03 \Omega \text{ cm}^2 \text{ h}^{-1}$, which reached a plateau at the end of the experiment. R_p 's degradation rate was relatively stable, ranging from $0.026 \Omega \text{ cm}^2 \text{ h}^{-1}$ in the beginning to $0.0261 \Omega \text{ cm}^2 \text{ h}^{-1}$ at the end of the experi-

ment. During the first 100 h of the study, R_s increased by about 53% and R_p about 185%, respectively.

The activation energies (E_a) were calculated from R_s and R_p values ($E_{a,Rs}$ and $E_{a,Rp}$, correspondingly). The activation energy changed only slightly during the electrochemical stability test conditions for both fuel cell and electrolysis modes (Table 3), indicating that changes occurred during the experiment in the conduction- and charge transfer mechanism in the material's bulk and on the surface, respectively. The changes were most likely caused by the segregation of some LSCMN components onto the surface. The segregation was made possible by a simultaneous change of B-site cations oxidation states, leading to changes in both the bulk and surface properties of LSCMN.

Table 3. Activation energies with standard deviations calculated from R_s and R_p in both fuel cell and electrolysis modes. The activation energies were calculated from Arrhenius plots within a temperature range from 650 to 800 °C.

	Duration (h)	$E_{a,Rs}$ (eV)	Std. deviation	$E_{a,Rp}$ (eV)	Std. deviation
Fuel cell mode (-0.8 V)	0	0.44	0.01	1.18	0.03
	48	0.44	0.02	0.97	0.04
	96	0.44	0.02	0.97	0.04
	150	0.46	0.02	1.00	0.04
Electrolysis mode (-1.5 V)	0	0.52	0.02	1.07	0.02
	48	0.47	0.01	1.03	0.02
	89	0.45	0.01	0.96	0.03
	130	0.44	0.02	0.93	0.03

There were multiple possible reasons for the increase of R_s during cell operation. One possible mechanism, which might cause the decrease of the electronic conductance (and, thus, increase in R_s) during the cell operation was the reduction of LSCMN. The reduction of the LSCMN electrode was expressed by a change of Mn^{4+} to Mn^{3+} and the simultaneous formation of oxide ion vacancies. Additionally, the decrease of the LSCMN matrix's electronic conductance was accompanied by a diminishing in the electrochemically active surface area. This kind of mechanism has also been demonstrated in the case of other electrode materials [121]. However, as it would be shown in *operando*-XRD measurements (see section 6.2.3), the lattice parameter (and, thus, also reduction of LSCMN B-site cations) changed rather quickly. This could be concluded from an observation that after switching the gas environment from oxidizing (air) to reducing (5% H_2), the lattice parameters remain constant after only a few hours. Thus, the change of the oxidation state of manganese and the formation of the oxide ion vacancies were both relatively quick processes. Hence, the slow

evolution of series resistance and its activation energy values was not caused only by the quick changes of conductance of MIEC, resulting from the oxide ion vacancy formation and the change of Mn's oxidation state.

The second mechanism, which could be considered as a reason for the change in R_s and $E_{a,Rs}$ is connected with a change of the porous electrolyte's ionic conductivity, which changes slowly in time because of the reduction of Ce^{4+} to Ce^{3+} in ScCeSZ electrolyte. Omar et al. [122] reported a 17.5% decrease in ionic conductivity during the first 250 h after introducing humidified hydrogen into the anode compartment at 600 °C. In our experiment, the decrease in conductivity according to this mechanism should reach the plateau much faster for several reasons. The samples used in our experiments were thinner, and the experiment was performed at a higher temperature (850 °C vs 600 °C), which both should lead to faster kinetics. In both modes (fuel cell and electrolysis), the limiting process which defines the R_s could not be the ionic conductivity of ScCeSZ since the activation energy of ScCeSZ ionic conductivity is about ~1 eV [123]. Variety of E_a values have been reported for LSCM ranging from 0.26 to 0.6 eV by different authors [45,124] depending on oxygen partial pressure. The value of $E_{a,Rs}$ in our experiment varied from 0.44 to 0.52 eV, which is characteristic of the LSCMN electrode at different oxygen partial pressures. Most likely, the main changes in R_s and $E_{a,Rs}$ are caused by the compositional changes of MIEC bulk material close to the MIEC|electrolyte and MIEC|gas interface.

Initial $E_{a,Rs}$ values of the electrode in fuel cell mode (0.45 eV) were slightly lower compared to initial activation energies of the similar electrode tested in electrolysis mode (0.52 eV). It was most likely caused by somewhat higher oxygen partial pressure in the porous electrode in the fuel cell mode, caused by H_2O generated on the electrode. This leads to an inference that the mass transport of reaction products (H_2O in fuel cell mode and H_2 in electrolysis mode) has been one of the main limiting stage of the total reaction. This statement was also confirmed by the fact that the $E_{a,Rs}$ in the electrolysis regime decreased along with the H_2 concentration in the porous electrode due to the electrochemical activity degradation. Additionally, $E_{a,Rs}$ in fuel cell regime started to increase if H_2O concentration in porous matrix decreases (because of loss of electrochemical performance).

The initial decrease of the $E_{a,Rp}$ in the fuel cell mode might be due to the continuous increase of active sites related to Ni particles' increased number on the surface due to Ni exsolution. After 150 h of operation in the fuel cell mode, the changes in surface eventually lead to less active surface sites and, correspondingly, an increase of E_a . Despite the initial decrease of $E_{a,Rp}$, the R_p values still increased during the whole stability test due to several reasons. Firstly, the area of active reaction sites diminished due to the formation of new nonactive phases on the surface. Secondly, the conductance of the MIEC LSCMN electrode (as can be concluded from the increase of R_s) decreased, which lead to the change of the electrochemical potential inhomogeneity across the LSCMN electrode.

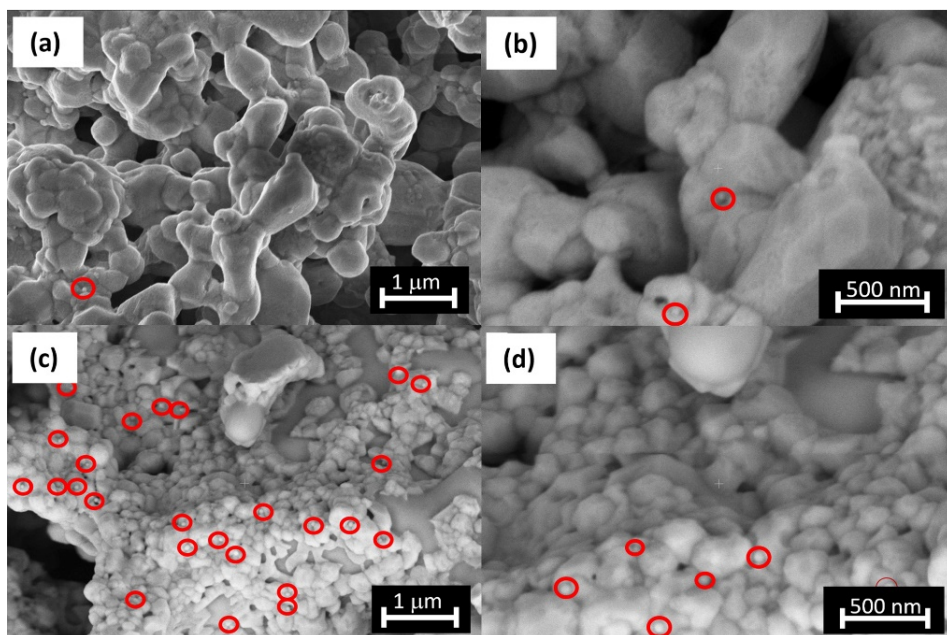


Figure 12. SEM images of the LSCMN fuel electrode, which were taken after the electrochemical stability test in the fuel cell mode (a and b) and in the electrolysis mode (c and d). Red circles were used to highlight the spherical particles that have formed during the electrolysis mode.

The LSCMN electrode microstructure changed during stability tests in both modes (Fig. 12). Based on the info in Fig. 12, the small (~ 50 nm) spherical particles appeared between the grains of the LSCMN electrode material after the operation in the fuel cell as well as in the electrolysis mode. In relative terms, the quantity of these new particles was higher on the surface of the electrode operated in the electrolysis mode. Similar particles were also observed from the PLD deposited nonporous electrode (after an operation in fuel cell mode), as described in the next chapter.

Additionally, the grain size of the LSCMN particles, which initially was 200–250 nm, increased during the operation in the fuel cell mode. This effect was most likely caused by partial coarsening of MIEC particles at fuel cell mode at 850 °C. The coarsening could lead to a decrease in the number of active sites and increased R_p . In addition, in some places in the porous electrode, partial delamination of LSCMN material from the ScCeSZ scaffold cannot be ruled out based on the SEM micrographs (Fig. 12c). This most probably happens during the initial intense degradation phase, where the R_s values increased rapidly at the beginning of the electrochemical experiment.

6.2.1. Electrochemical stability tests of nonporous PLD electrode

The performance of the nonporous LSCMN electrode deposited using the PLD method degraded even faster than the infiltrated electrode – during the first 40 h of cell operation (Fig. 13), the value of R_p increased from $0.2 \Omega \text{ cm}^2$ to $0.7 \Omega \text{ cm}^2$. After this initial rapid loss of performance, the R_p continued to increase with an approximate rate of $0.014 \Omega \text{ cm}^2 \text{ h}^{-1}$. Even though the system stabilizes at the end of the experiment, the total increase of R_p of nonporous LSCMN electrode was even more severe than in the case of infiltrated porous electrodes. At the same time, R_s of the PLD electrode was more stable – increased only about 12% with 80 h of cell operation. At about 20 h of the electrochemical testing, the measurements of impedance at different temperatures and gas compositions were performed. Measurements at higher oxygen partial pressures lead to a decrease of R_s , which was most likely related to the regeneration of ceramic LSCMN electrode with an increase of p_{O_2} [64].

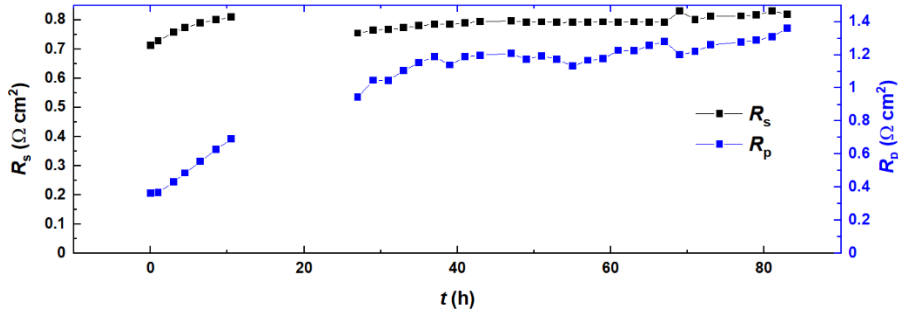


Figure 13. The dependence of R_s and R_p of the PLD deposited LSCMN electrode on time of duration of the electrochemical stability test measured at 850 °C at open-circuit voltage, OCV (97% H_2 / 3% H_2O gas atmosphere) using the 3-electrode configuration.

The spherical particles previously seen on the porous LSCMN electrodes (Fig. 12) also had formed on the surface of PLD electrode with cell operation (Fig. 14).

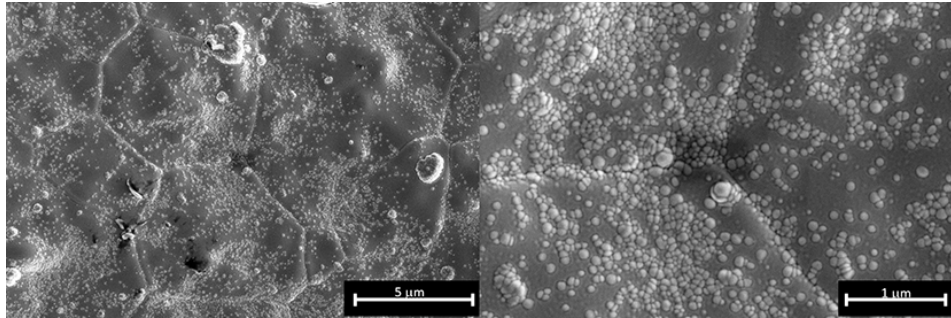


Figure 14. SEM images of PLD deposited LSCMN fuel electrode after electrochemical tests at fuel cell mode.

To determine the phase formed on the PLD electrode, Grazing incidence X-ray diffraction (GI-XRD) analysis has been performed. New reflections appeared at 31.3° , 33.5° (very low intensity) and 39.4° , which probably corresponded to the new phase located at the surface of the electrode, seen in Fig. 14, since the relative intensities of these reflections do not change remarkably when smaller incidence angles (ϕ) were used. The Bragg peak at 31.3° corresponds to the Ruddlesden Popper phase of LSCMN (PDF 04-013-5750). The phase causing the reflection at 39.4° remains unidentified. The Bragg peaks at 22.8° , 32.5° , 40.1° , 46.55° , 52.47° , 58.0° , and 68° were also observed in the deeper layers of the electrode and was assigned to LSCMN. These reflections are labelled by Miller indices in the Fig. 15.

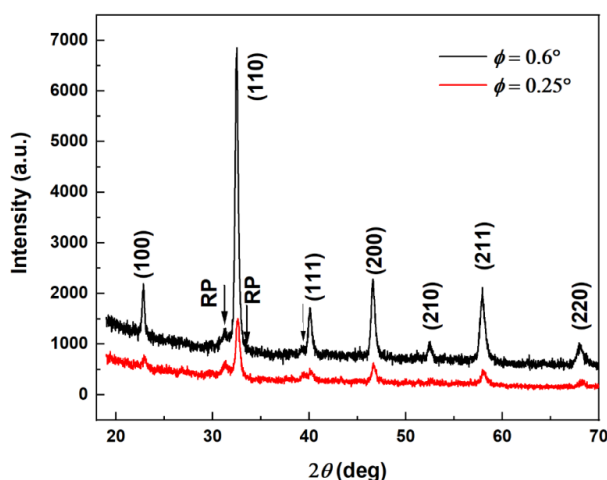


Figure 15. GI-XRD diffractogram of the nonporous PLD deposited LSCMN electrode measured at room temperature in air at $\phi = 0.25^\circ$ (red line) and 0.6° (black line). The reflections of LSCMN with perovskite structure were labelled by Miller indices in the figure. The arrows indicate phases that are mostly on the surface of the electrode, and reflections labelled as “RP” correspond to most likely a Ruddlesden-Popper phase.

6.2.2. Influence of the redox cycle on the performance of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ electrode

After measuring the initial degradation of porous LSCMN electrodes, the redox cycle was performed to clarify the reversibility of the degradation process (the layout of the experiment is seen in Fig. 5). During the reoxidation process of the LSCMN electrode, its electrochemical performance partially recovered (Fig. 16) – the R_s and R_p values decreased. The partial regeneration of the full-ceramic electrode with the redox cycle has also been shown in previous studies [64].

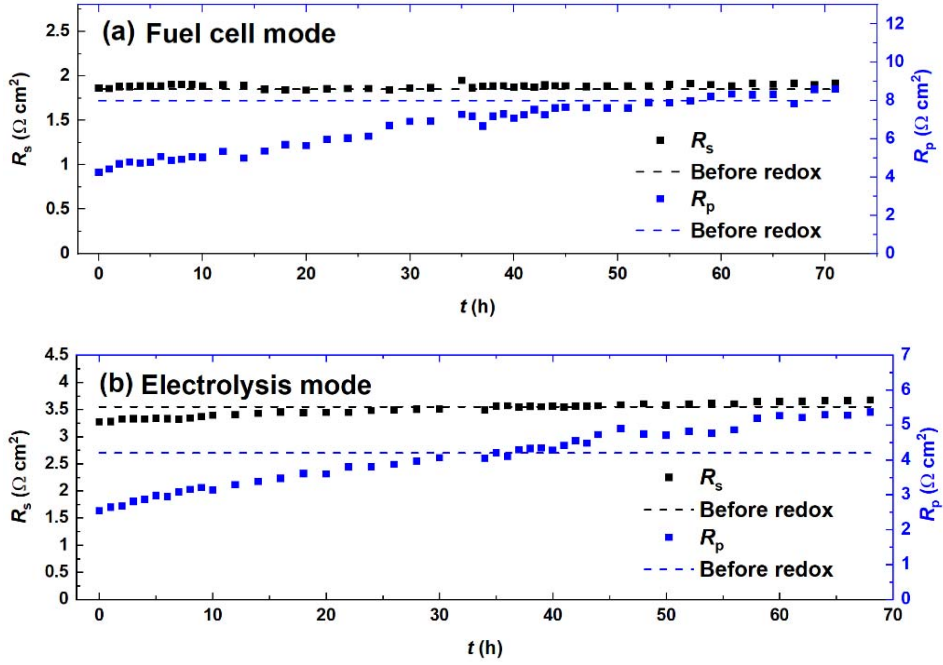


Figure 16. The dependence of R_s and R_p values on time after the redox cycle. The cells operated at 850 °C (a) in fuel cell mode (−0.8 V, 97% H_2 / 3% H_2O gas atmosphere) and (b) in electrolysis mode (−1.5 V, 70% H_2 / 30% H_2O gas atmosphere). The dashed lines represent R_s and R_p values before the redox cycle.

As follows from Fig. 16, the influence of the redox cycle on the catalytic activity was slightly different for electrodes operated at different gas- and electrochemical conditions. For the electrode operated in the fuel cell mode, we did not observe the change of R_s because of the redox cycle. However, partial regeneration of R_s (conductivity) was observed in the electrode operated in the electrolysis mode.

Based on the fact that the R_s of the electrode operating in the fuel cell mode did not decrease during the redox cycle, it could be confirmed that in the case of the ScCeSZ/LSCMN electrolyte|electrode system, the R_s was not defined by any process related to the ionic conductivity of ScCeSZ. Since the changes in the ionic conductivity of ScCeSZ (more specifically, the equilibria between Ce^{4+} and Ce^{3+}) caused by the redox environment should have appeared similarly and reversibly in the case of both electrodes (fuel cell and electrolysis mode). Most likely, a slight recovery of R_s for the electrode operated in the electrolysis mode was related to the change of properties of LSCMN.

More significant changes with the redox cycle could be observed in the R_p value. The decrease of R_p with conducted redox cycle in the case of electrode operated in the fuel cell mode was 48% and in the case of electrolysis electrode

41%. When the R_p values from the beginning of the experiment and after the redox cycle are compared, the R_p has increased by 512% in the fuel cell mode and 486% in the electrolysis mode. So, the recovery was relatively modest – most of the degradation was non-reversible.

After the partial regeneration of electrodes during the redox cycle, the electrochemical performance of the electrode started to degrade again and even faster than before the redox cycle.

The partial recovery of the initial R_p during reoxidation has been explained by oxidative incorporation of exsolved components into the LSCMN phase [125]. However, the decomposed phase did not recover fully with the change of the p_{O_2} , and thermal treatment at much higher temperatures is necessary for that.

6.2.3. *Operando* EC-HT-XRD in fuel cell mode

Operando EC-HT-XRD characterization was performed for simultaneous study of the crystallographic and electrochemical changes in the LSCMN electrode during the degradation processes at fuel cell operating conditions. Lattice parameters of LSCMN and ScCeSZ in porous SOC electrode under different electrochemical conditions and different gas atmospheres (OCV and -0.8 V were the electrochemical conditions; synthetic air, humidified 5% H_2 in He and humidified 10% H_2 in He were the gas atmospheres) were observed.

One of the most significant discoveries from the *operando* XRD experiment was the substantial increase in the lattice parameter of ScCeSZ electrolyte, a_{ScCeSZ} , during the experiment (Fig. 17). After a relatively quick initial increase of a_{ScCeSZ} (approximately first 250 min of operation), a slow, approximately linear continuous increase appeared. The reduction of Ce^{4+} to Ce^{3+} in the ScCeSZ electrolyte could partially explain the lattice's initial expansion. The oxidation state of Ce takes place due to the shift of the gas environment from oxidizing air atmosphere at the start of the experiment to reducing atmosphere of 5% H_2 . During this process, p_{O_2} in the fuel electrode chamber decreased from 0.2 to $1.5 \cdot 10^{-18}$ atm.

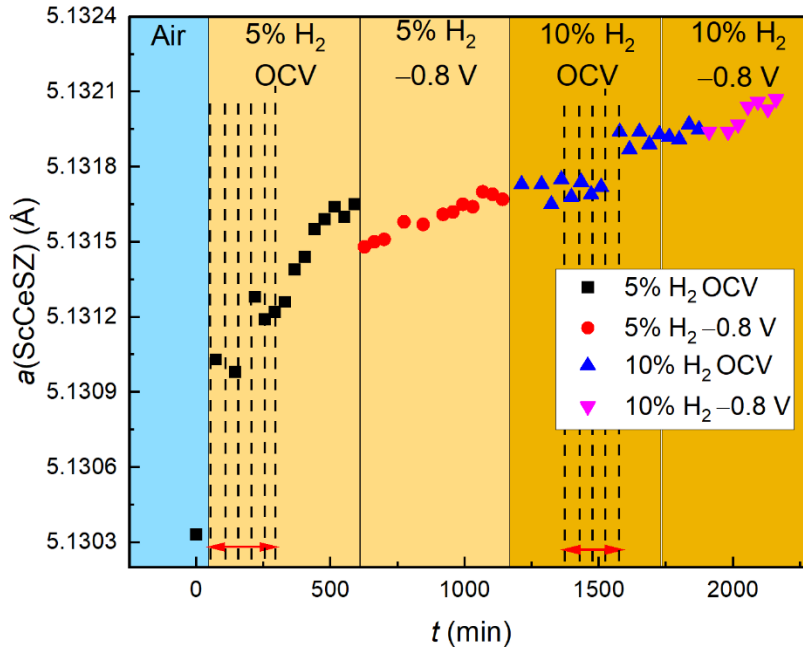


Figure 17. Dependence of ScCeSZ lattice parameter, a_{ScCeSZ} , on time at different gas atmospheres and electrochemical conditions (shown in the figure). At the start of the test, the gas environment was changed from air to 5% H_2 and then after some time to 10% H_2 ; electrochemical conditions were also changed from OCV to -0.8 V during cell operation. Red arrows show the regions of thermal instability caused by the change of the gas environment.

The real p_{O_2} in the porous electrode (at the surface of ScCeSZ as well as LSCMN) depended on both the gas environment in the electrode compartment and the polarization of the electrode, i.e., on oxide ion flux from cathode to anode. Thus, using the in-house developed dual-chamber *operando* XRD cell, we can measure the p_{O_2} at the fuel electrode's surface by monitoring the OCV of the cell.

Based on the monitoring of the OCV value, which reflects p_{O_2} in the fuel electrode room, we concluded that the gas environment change from oxidizing to reducing was very fast. Namely, the OCV was stable already 25 min after the change from air to 5% H_2 at the start of the experiment. Moreover, it took only 8 min for OCV to stabilize after the change from 5% H_2 to 10 % H_2 . Thus, the continuous increase of the a_{ScCeSZ} was not due to the slow change of gas atmosphere in the pores but rather by diffusion processes of oxide ions and defects in porous and dense layers of electrolyte accompanying the Ce^{4+} reduction. The diffusion of oxide ions take a relatively long time due to the considerable change in p_{O_2} and because the dense electrolyte also needs to adapt to this condition.

In the *operando* study of Ni-GDC (chapter 6.1) increase in the a_{ScCeSZ} during the first 1000 min of cell operation at 650 °C was also observed when the gas phase composition was changed from air to 1% H₂. We attributed the increase to the change of the oxidation state of Ce in ScCeSZ from Ce⁴⁺ to Ce³⁺. The reduction of Ce in the ScCeSZ lattice was relatively slow in the Ni-GDC study (1000 min) in comparison to the current study (250 min). This was likely due to the lower temperature applied, 650 °C vs 850 °C. Anyhow, after this initial increase, the a_{ScCeSZ} remained constant in the Ni-GDC study. However, in our study with the LSCMN as a fuel electrode, the a_{ScCeSZ} kept increasing during the whole experiment. We can explain the quick initial increase of the lattice parameter during 250 min with the change of Ce's oxidation state in ScCeSZ, but the origin of the further increase must lie elsewhere.

The relatively small changes in the experimental conditions have a rapid effect on the a_{ScCeSZ} , which could be seen in the changes of a_{ScCeSZ} happening at 626 min, 1212 min, and 1910 min (Fig. 17). The reason for this being the changes' influence on the p_{O_2} in the porous electrode, like when OCV is changed to -0.8 V potential and gas atmosphere from 5% to 10% H₂. As the electrode activity decreases due to its degradation, the magnitude of lattice parameter change related to changes in experimental conditions also decreases in time. Instability of the system could be observed when changing the gas environment (the change of gas phase from air to 5% H₂ at the start of the experiment and the subsequent change from 5% H₂ to 10% H₂), which is caused by the change of the heat capacitance and thermal conductivity of gas mixture. Even small changes in the thermal balance around the *operando* setup lead to a shift of the electrode's surface level. Since the surface level was calibrated for the XRD measurement, the shift of the surface level causes shifts in the XRD pattern and, thus, also in the lattice parameter. Therefore, some inconsistencies were seen in the a_{ScCeSZ} values directly after changing the gas composition.

The LSCMN lattice parameters increased significantly after changing the gas atmosphere from air to 5% H₂ in He at 850 °C. However, it remained at a constant level after approximately 200 minutes (Fig. 18). During the initial gas changing process, the speed of the lattice parameter changes, a_{LSCMN} and c_{LSCMN} , was suppressed by the processes taking place in ScCeSZ (release of oxygen if Ce⁴⁺ was reduced to Ce³⁺ in the electrolyte). Release of oxygen from ScCeSZ decreases the reduction speed of LSCMN or, in other words, also defines the speed of the LSCMN reduction process. The increase of lattice parameters of LSCMN had been caused by the formation of oxide ion vacancies and by the reduction of B-site cations. When the gas atmosphere was changed from 5% H₂ in He to 10% H₂ in He, the a_{LSCMN} increased from 5.5521 Å to 5.5540 and c_{LSCMN} from 13.645 Å to 13.659 Å. These lattice parameter changes indicate that a slight decrease in oxygen partial pressure leads to an additional reduction of B-site cations in LSCMN.

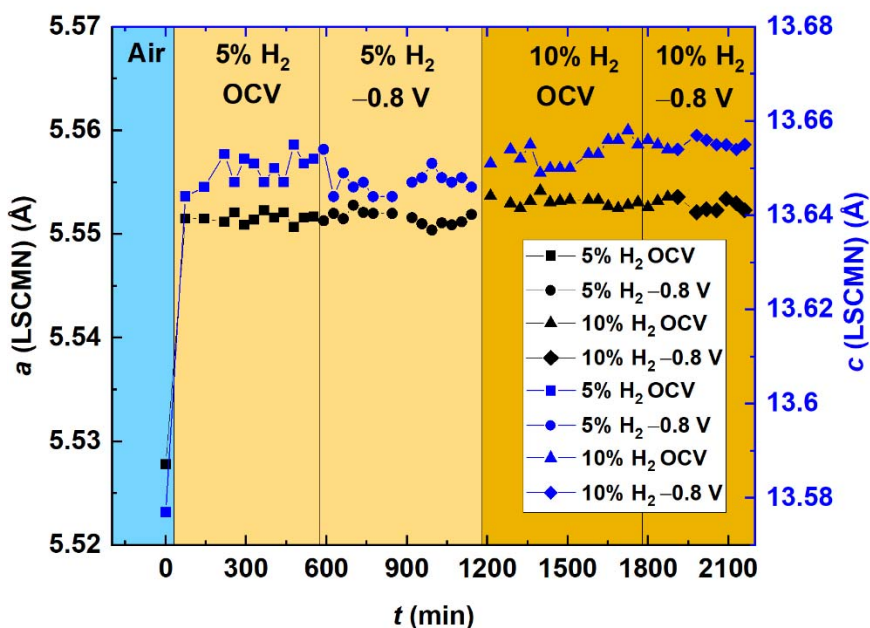


Figure 18. Dependence of LSCMN lattice parameters (a and c) on dwelling time after a change of gas environment from air to reducing (5% H₂ in He and 10% H₂ in He) atmosphere at 850 °C and at OCV conditions and under polarization (–0.8 V).

The lattice parameters changed slightly when the cell has been polarized from OCV to –0.8V in a 5% H₂ atmosphere. The change could be seen from the second measurement point. However, these changes caused by operation conditions (temperature and electrode polarization) were not statistically significant.

To changes of LSCMN lattice parameters would be more significant if the electrode activity would be higher and if higher H₂ concentrations were used. More water is produced at higher current densities, i.e. higher oxygen partial pressures will be generated, leading to more significant changes in lattice parameters.

In Fig. 19, two diffractograms were presented that were measured in the same atmosphere (95% He and 5% H₂) and with the same measurement setup. However, one was measured in the early stages of the experiment and the second at the final stage of the experiment. According to the calculations made from these diffractograms, the wt% of the LSCMN phase had decreased by 27±4,5% during the experiment. Thus, the electrode degradation is one of the main reasons why we can see a significant increase in R_p and R_s (Fig. 11). The high uncertainty is due to the different integral intensity changes of different LSCMN reflexes – most likely, the atomic occupancy of LSCMN changes during electrode degradation.

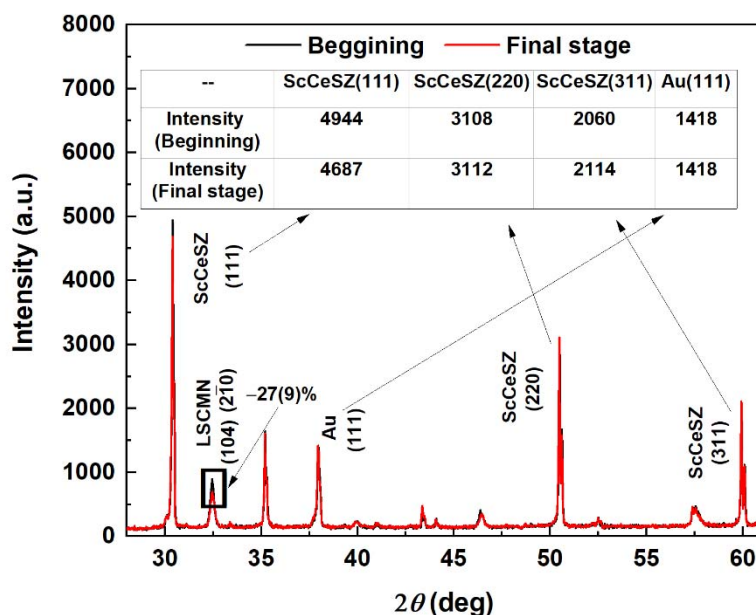


Figure 19. Diffractogram measured at the beginning of the *operando* experiment (black line) and the final stage of the experiment (red line) measured in the same setup and same gas atmosphere (5% H₂ and 10% H₂ in He). The table in the graph shows the intensities of different ScCeSZ maxima and gold (111) reflex for comparison.

The changes in the Bragg peaks of the ScCeSZ lattice also indicate the change in its atomic occupancy. More specifically, the intensity of the (111) ScCeSZ maximum has decreased, while (220) and (311) have increased (the table in Fig. 19). This theory was validated by the fact that intensities of gold maxima did not change, as can be seen from the table in Fig. 19. Therefore, the ever-continuing increase in the ScCeSZ lattice parameter, a_{ScCeSZ} , discussed previously (Fig. 17), can be explained by the continuous changes in the atomic occupancy of the ScCeSZ lattice. Since the wt% of the LSCMN phase considerably decreased during the course of the experiment, while the a_{ScCeSZ} continuously increased, it was reasonable to conclude that some LSCMN degradation product starts to dope the ScCeSZ lattice. Unfortunately, the whole pattern fit was not good enough to conclude neither qualitatively nor quantitatively which elements concentration had changed in the lattice.

6.3. $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ SOC fuel electrode

6.3.1. Physical characterization

Diffraction patterns in Fig. 20 correspond to different LSCNT-x compositions, where, generally, the LSCNT perovskite-type phase dominates only. Very low-intensity Bragg peaks attributed to NiO secondary phase can be distinguished in LSCNT-10 and LSCNT-20 diffraction patterns, respectively.

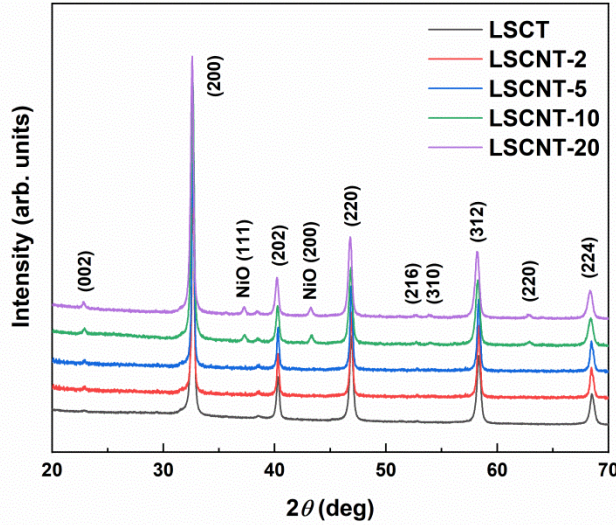


Figure 20. Diffraction patterns of $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ powders in the air at room temperature. Reflections were labelled by Miller indices in figure.

In situ XRD measurements at elevated temperatures were performed (Fig. 21) to understand how Ni concentration in LSCNT-x B-site influences the lattice parameters in different gas atmospheres (oxidizing and reducing atmosphere). A general trend is that doping of LSCNT with Ni increases the unit cell volume (Fig. 21a). This phenomenon is related to the difference in the increase of oxide ion vacancies and ionic radii of B-site cation – Ni^{2+} (0.690 Å) radii is greater than Ti^{4+} (0.605 Å). It appears from Fig. 21a that in the concentration range from 0 to 10% Ni in the LSCNT-x B-site, the lattice expands almost linearly. The lattice expansion slows down when Ni-content is increased even further, which leads to an inference that there is a limit of Ni solubility in the LSCNT lattice's B-site. Even though LSCNT-10 follows similar linear dependence between Ni concentration and unit cell volumes (Fig. 21a) like LSCNT, LSCNT-2, and LSCNT-5 materials, a detectable amount of NiO has appeared in the diffraction pattern (Fig. 20). The qualitatively different pattern for LSCNT-10 and LSCNT-20 compared to LSCNT-2 and LSCNT-5 in Fig. 21b also indicates

limitations to adopt the Ni in perovskite lattice, which lead to qualitative changes of bulk material properties. However, Fig. 21 shows increased lattice volume for LSCNT-20 compared to LSCNT-10, indicating no precise saturation concentration for Ni. There is an equilibrium between dissolved Ni in the LSCNT-x lattice and Ni in NiO.

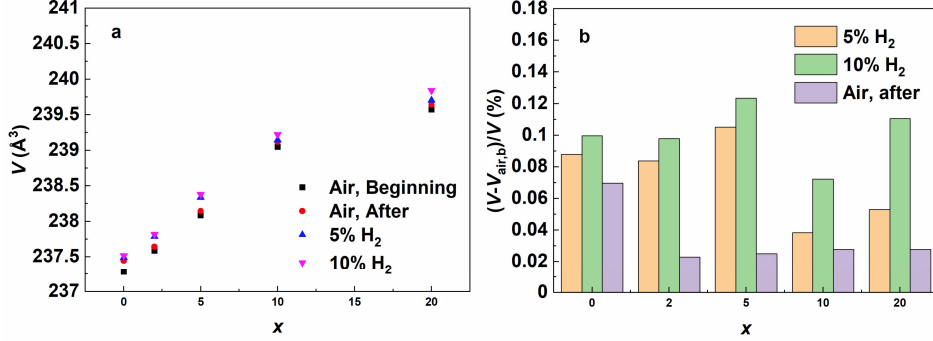


Figure 21. Dependence of unit cell volume of $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ on Ni content (a) and corresponding changes of unit cell volumes (b) caused by changes in gas conditions compared to the initial situation in synthetic air. XRD characterization was performed at *in-situ* conditions at 800 °C in synthetic air (initial situation and after re-oxidation) and in humidified 5% H₂ 95% N₂ and humidified 10% H₂ 90% N₂.

The change of the gas atmosphere from air to humidified 5% or 10% H₂ (in N₂), caused an increase of the LSCNT-x lattice volume (Fig. 21). At higher H₂ concentrations, the lattice expands even further. This phenomenon can be explained by equation 19 and 20. The reducing atmosphere with low oxygen partial pressure lead to the release of lattice oxygen to the gas phase and creates electron carriers. Release of oxygen from perovskite lattice causes the creation of oxide ion vacancies and reduction of Ti^{4+} to Ti^{3+} , which has a higher ionic radius compared to Ti^{4+} .

$$\text{O}_\text{O}^x \rightleftharpoons 2e' + \frac{1}{2}\text{O}_2 + V_\text{O}^{\cdot\cdot} \quad (19)$$

$$e' + \text{Ti}_{\text{Ti}}^x \rightleftharpoons \text{Ti}_{\text{Ti}}' \quad (20)$$

The $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple makes n-type semiconduction possible in these materials [126]. Comparing the changes in unit cell volume in the air atmosphere before the experiment and after the first redox cycle (Fig. 21b) indicated that irreversible processes occur during the reduction and/or re-oxidation of the electrode under study. The most notable irreversible changes occur in undoped LSCT, while in all other doping levels, irreversible volumetric changes stay

almost at the same level. It is very likely, that irreversible crystallographic changes in studied materials are caused by partial irreversible reduction of Ti^{4+} to Ti^{3+} , described by Canales-Vázquez et al. [127]. The Ni-doped materials' improved reversibility compared to Ni-free LSCT might be caused by Ni's influence on the LSCNT-x lattice parameter or its exsolution from the lattice or better reversibility of $\text{Ni}^{3+}/\text{Ni}^{2+}$. Exsolution of Ni from lattice leads to a slight decrease in the lattice parameter. In parallel with lattice expansion (caused by reduction of Ti^{4+} to Ti^{3+}), it could be seen as a suppressed nonreversible expansion [128].

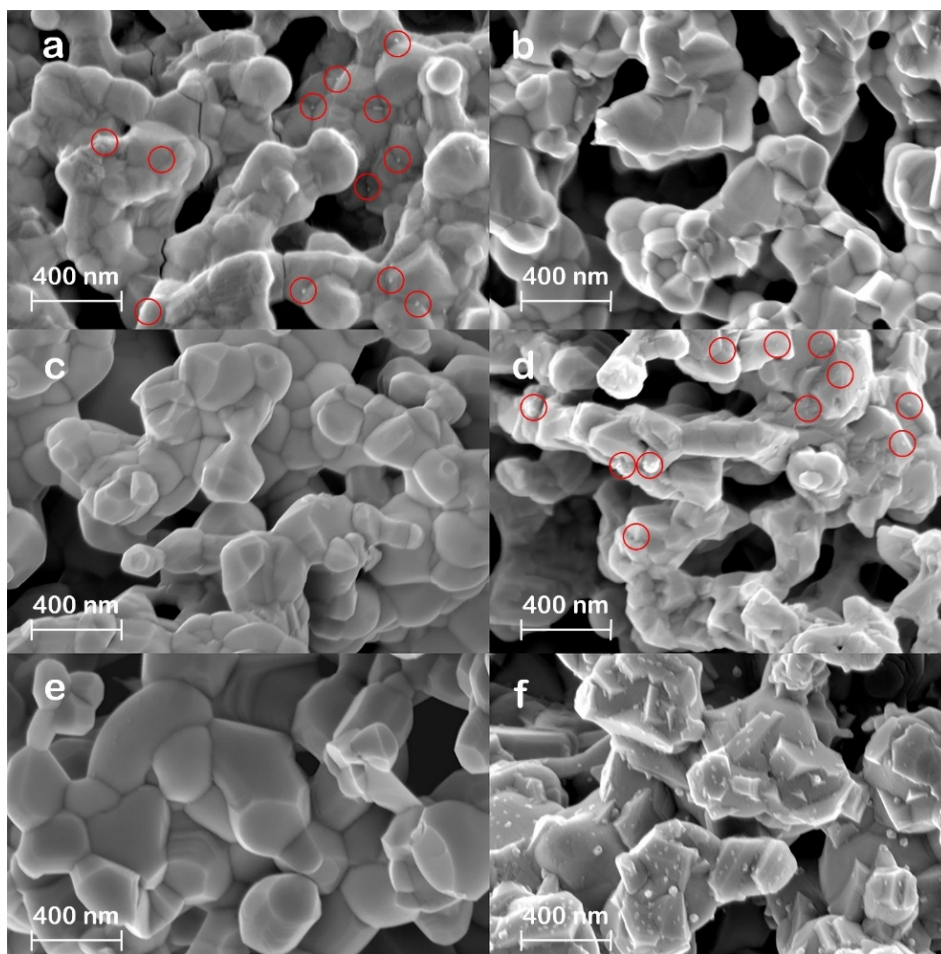


Figure 22. SEM images of porous $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{TiO}_{3-\delta}$ (LSCT) (a and b), $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (LSCNT-5) (c and d) and $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSCNT-20) (e and f) electrodes after sintering in air (a, c, e) and after 100 h treatment in humidified H_2 (97% H_2 3% H_2O) atmosphere at 900 °C (b, d, f).

In Fig. 22, SEM images of as-sintered in the air and reduced (100 h in 97% H₂ 3% H₂O atmosphere at 900 °C) LSCT, LSCNT-5 and LSCNT-20 electrodes are presented. Based on info in Fig. 12, small particles can be seen on the reduced Ni-doped electrodes' surface (Fig. 22a, 22d, 22f). These tiny particles on LSCNT-5 have diameters of approximately 10-20 nm and significantly more particles on LSCNT-20 (Fig 22f) with 10-45 nm size. These particles were not visible in electrodes that had not been reduced. The increase of Ni-content in the electrode increased the quantity and size of particles expressed on the electrode surface. Comparison of La_{0.25}Sr_{0.25}Ca_{0.4}Ti_{0.8}Ni_{0.2}O_{3-δ} electrodes' XPS spectral intensities of Ni 3p and Ti 3s maxima collected before and after reduction (Fig. 23) leads to a conclusion that reduction caused an increase of Ni concentration on the electrode surface. According to XPS analysis, the Ni in the surface of reduced La_{0.25}Sr_{0.25}Ca_{0.4}Ti_{1-x}Ni_xO_{3-δ} lattice is dominantly in the metallic form (Fig. 23a), as has been described in several papers studying exsolution [67,75, 128,129]. A slight signal from oxidized Ni (Fig. 23a) could be attributed to a slightly oxidized surface layer of precipitated Ni-particles or for the Ni in the perovskite lattice.

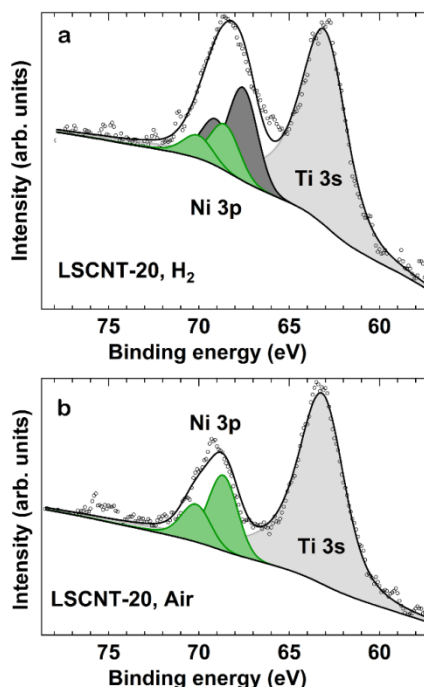


Figure 23. Comparison of Ni 3p and Ti 3s fitted XPS spectra measured from the surface of as-sintered (non-reduced) (a) and reduced (100 h in 97% H₂ 3% H₂O atmosphere at 900 °C) La_{0.25}Sr_{0.25}Ca_{0.4}Ti_{0.8}Ni_{0.2}O_{3-δ} sample (b). Dots correspond to experimental data and curve to fitted spectra and the black line under the curve to baseline. Under the maxima, the bell-shapes correspond to different contributions – green to oxidious Ni, dark grey to metallic Ni and light grey to Ti.

Several small spherical particles were detectable on the surface of as-sintered (non-reduced) LSCT (Fig. 22a). Most likely, these particles consisted of CaO or some other more complex Ca-rich oxide phase. This claim was supported by XPS analysis of as-sintered LSCT and reduced LSCT, where higher Ca concentration on LSCT surface of as-sintered electrode compared to the reduced LSCT surface (Fig. 24a) had been observed. In Ni-doped materials, no such dependence between the gas environment and Ca concentration at the electrode surface was detected (Fig. 24b). Behaviour, as mentioned above, indicates that Ca-mobility in LSCT can be suppressed with Ni-doping.

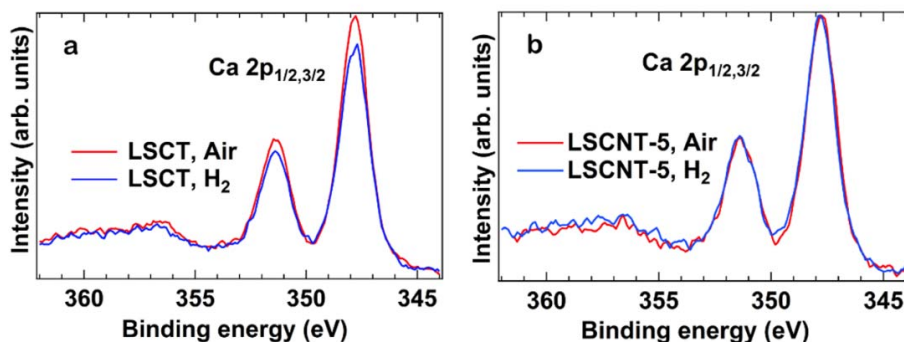


Figure. 24 Ca 2p electron spectra of $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{TiO}_{3-\delta}$ (a) and $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (b), measured at the surface of reduced electrode (100 h in 97% H_2 3% H_2O atmosphere at 900 °C) indicated as “ H_2 ” and pristine (as-sintered) electrode indicated as “Air” in figure.

As could be seen in Fig. 23, the LSCNT-x grain size in porous electrodes is influenced by Ni concentration. An increase of Ni concentration in LSCNT-x causes an increase of grain size if electrodes are sintered at the same temperature, which means that sinterability has been improved with an increase of Ni concentration. This observation implies that the surface area and pore size distribution are also slightly affected by the Ni concentration in the electrode material. A similar effect has also been studied by Yagub et al. [70].

As can be seen from data in Fig. 25, the La/Sr ratio expressed on the surface is dependent on the Ni-concentration in the lattice. One possible explanation could be that Ni-doping in LSCNT-x electrode ($\text{Ni}^{2+}/\text{Ni}^{3+}$ ion substitutes $\text{Ti}^{3+}/\text{Ti}^{4+}$ ion) lead to an increase of the oxide ion vacancies, which resulted in a change of material properties so that A-site cations were bound more firmly to the lattice. La^{3+} -ion with a higher charge than Sr^{2+} was even more firmly bound to the lattice than Sr^{2+} -ion [60,130]. Moreover, Sr^{2+} with high ionic radii compared to La^{3+} ion has a tendency to segregate onto the surface since larger A-site perovskite dopants cause more elastic energy in the lattice [60,130]. This means

that the increase of Ni-content in the bulk LSCNT-x electrode leads not only to a higher Ni concentration but also to a decrease of the La/Sr ratio appears on the surface.

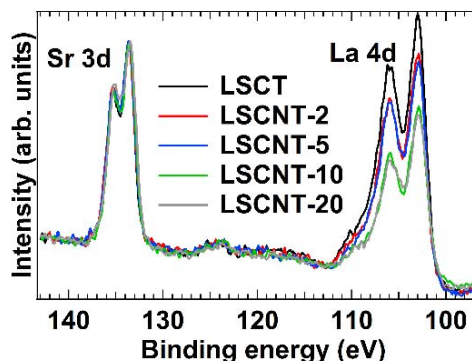


Figure 25 Sr 3d and La 4d photoelectron spectra for reduced (100 h in 97% H₂, 3% H₂O atmosphere at 900 °C) La_{0.25}Sr_{0.25}Ca_{0.4}Ti_{1-x}Ni_xO_{3-δ} (x = 0, 0.02, 0.05, 0.1 or 0.2) electrodes with different Ni doping levels.

Stabilizing effect of Ni-doping on the A-site cations was also confirmed by SIMS measurements (Fig. 26). For undoped LSCT material sintered at 1250 °C, Sr's accumulation and the formation of SrZrO₃ phase between GDC barrier layer and ScCeSZ electrolyte [131] have been observed (Fig. 26b). LSCT doping with Ni suppresses the Sr mobility and accumulation of Sr to the interlayer between GDC and electrolyte (Fig. 26c,d). Sr-mobility during the processing of electrodes made from pure LSCT was suppressed by decreasing the sintering temperature from 1250 °C to 1100 °C (Fig. 26f). However, sintering at 1100 °C doesn't give sufficient contact between the LSCT electrode and the chemical barrier layer.

Thus, Ni-free LSCT electrodes electrochemical measurements will not be reported in the next section because of the reasons mentioned above. LSCT powder with a smaller particle size is essential for lowering the sintering temperature.

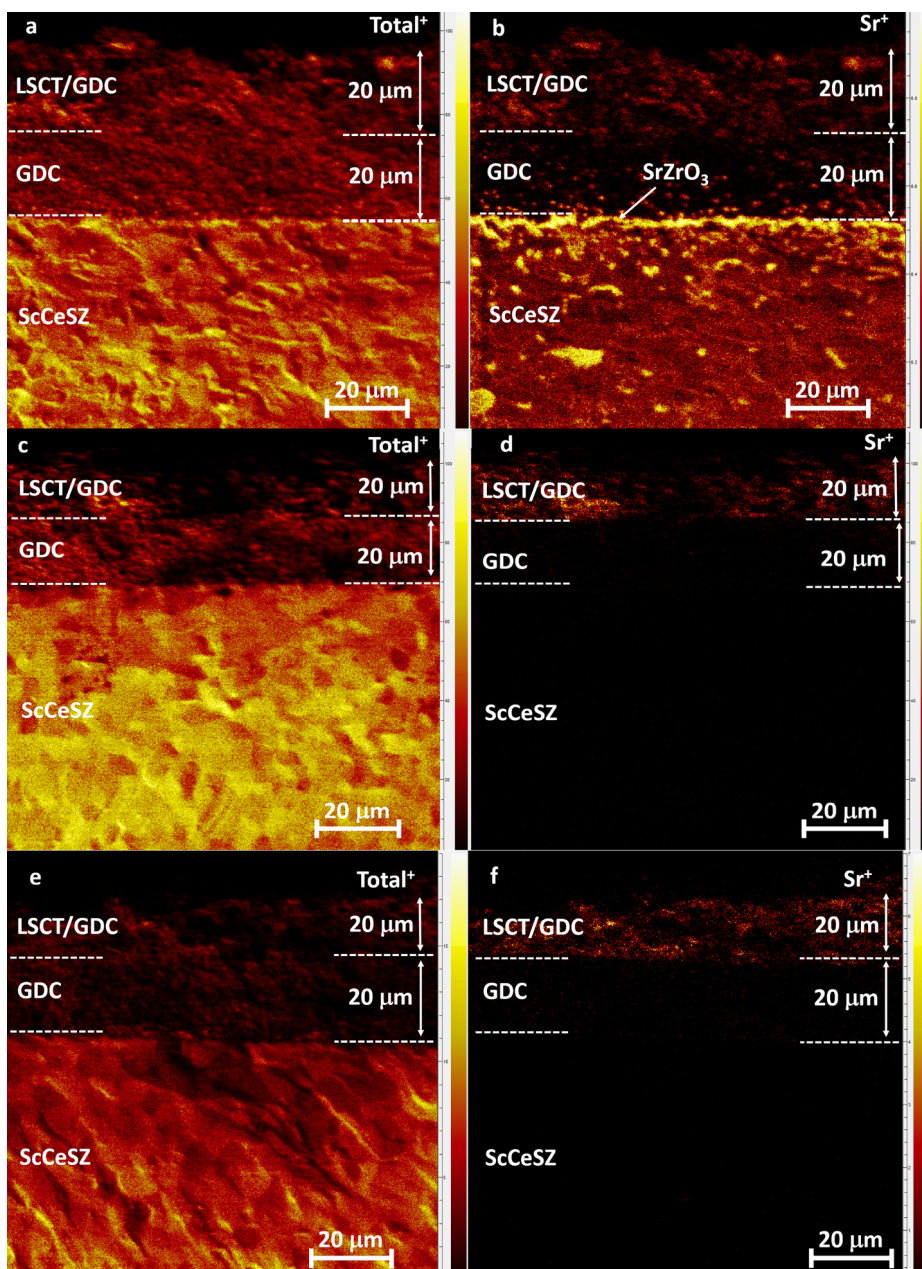


Figure 26. FIB-TOF-SIMS analysis results of fuel electrode side cross-sections from selected cells. In the left column total cation images (a, c, e) and in the right side Sr^+ -images (b, d, f) are presented for $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{TiO}_{3-\delta}$ (LSCT) sintered at 1250 °C (a and b); $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ sintered at 1250 °C (c and d) and for LSCT sintered at 1100 °C (e and f).

6.3.2. Electrochemical analysis

The electrochemical impedance analysis has been carried out to measure its activity and identify the nature of the factors limiting LSCNT-x electrodes' performance. The series resistance (R_s) and polarization resistance (R_p) values were determined from Nyquist plots. An equivalent circuit of $R_s(R_2CPE_2)(R_3CPE_3)$ (Fig. 27) was used for fitting at the LSCNT-2 and LSCNT-5 Nyquist plots. LSCNT-10 and LSCNT-20 electrodes theoretical impedance spectra were calculated using an equivalent circuit consisting of $R_s(R_1CPE_1)(R_2CPE_2)(R_3CPE_3)$ (Fig. 27) equivalent circuit was used. The R_p value could also be calculated from R_1 , R_2 and R_3 as a sum of these.

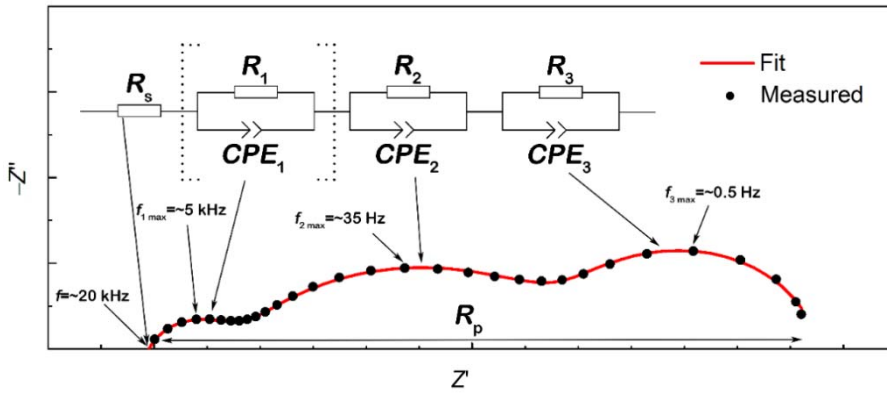


Figure 27. The equivalent circuit used for fitting of the calculated impedance spectra and to the experimentally measured Nyquist plot (black dots) with the fitting result (red line) are presented in the Fig. Characteristic relaxation frequencies determined from the Nyquist plot arc maxima for high- ($f_{1 \text{ max}}$), mid- ($f_{2 \text{ max}}$), and low- ($f_{3 \text{ max}}$) frequency processes are shown in the drawing. R denotes resistance, and CPE means a constant phase element.

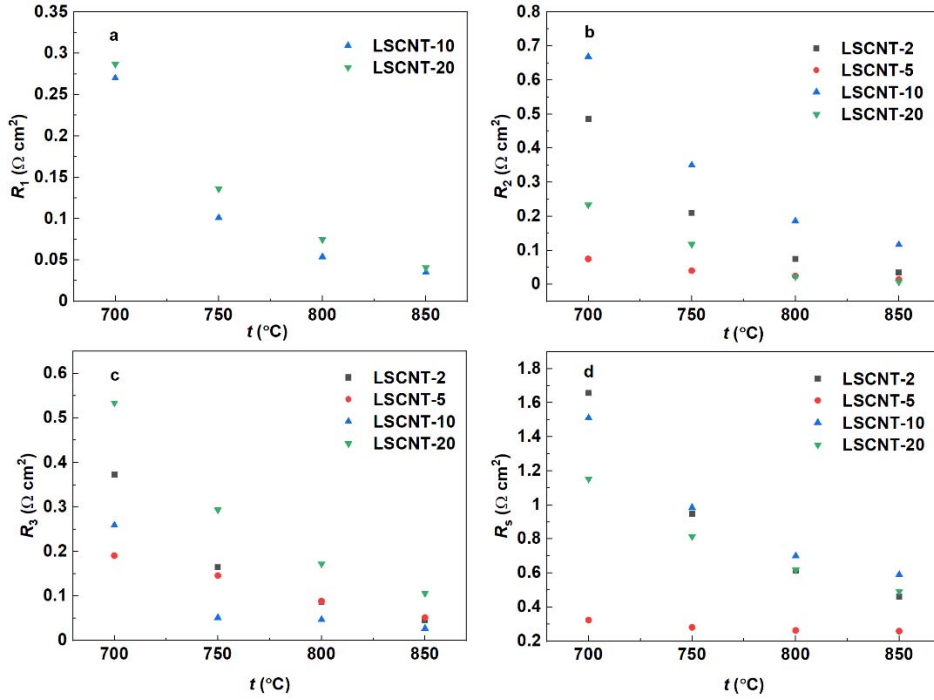


Figure 28. Temperature dependence of R_1 (a), R_2 (b), R_3 (c) and R_s (d) for $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0.02, 0.05, 0.1$ or 0.2) electrode at $850\text{ }^\circ\text{C}$ in $97\% \text{H}_2$, $3\% \text{H}_2\text{O}$ gas atmosphere measured at -0.9 V vs ref.

In LSCNT-10 and LSCNT-20 impedance spectra, a high-frequency semicircle ($-R_1\text{CPE}_1-$) appeared. The relaxation frequency, $f_{1\text{ max}}$, of this limiting process was in the range of 4–23 kHz (Table 3), depending on temperature and material characteristics. The real part of the impedance varied from 0.035 to $0.287\text{ }\Omega\text{ cm}^2$ at different temperatures (Fig. 28). The previous chapter demonstrated that in LSCNT-10 and LSCNT-20, separate Ni or NiO phase (Fig. 20) exists in the bulk of the material. This limiting process is likely connected with the increased resistance in the grain boundary region because of excess Ni as the high-frequency semicircle appears only in the materials that clearly show Ni excess (Fig. 28a). The Ni-rich phase most likely does not appear only on the outer surface but also in the grain boundary interface of the LSCNT- x material, where it might act as an internal barrier for ionic transport. This process's relaxation frequency range is similar to the relaxation frequencies of limiting the grain boundary process in nanocrystalline zirconia presented in the literature [132]. Also, activation energies of the high-frequency process, $E_{a,R1}$, in LSCNT- x MIEC material (1.22 – 1.28 eV) are very similar for activation energies of ionic transport through contaminated grain boundary interface presented in the literature (1.20 – 1.26 eV) [132,133]. In conclusion, based on the information above, in the case of high Ni concentrations (10% and higher) in LSCNT- x , the Ni

starts to segregate to the grain boundary region, which suppresses the oxide ion transport through the grain boundary.

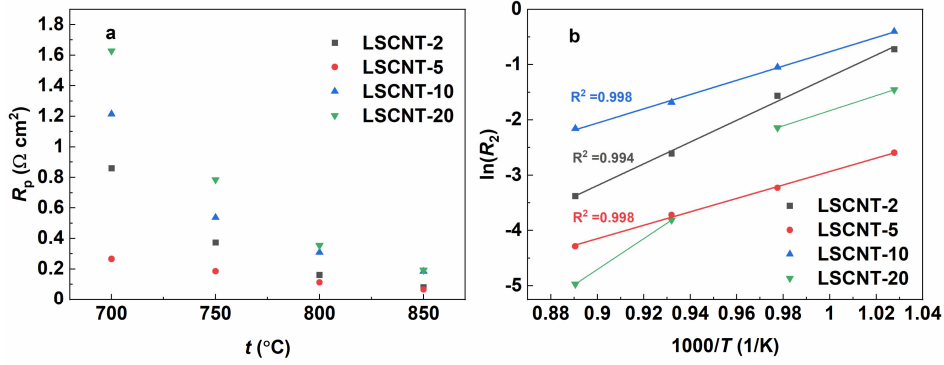


Figure 29. Temperature dependence of R_p (a) and $\ln(R_2)$ (b) for $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0.02, 0.05, 0.1$ or 0.2) electrode at 850°C in 97% H_2 /3% H_2O gas atmosphere measured at -0.9 V vs ref.

The mid-frequency semicircle ($-R_2\text{CPE}_2-$) appeared in all the studied materials. This process's characteristic relaxation frequency varies from 25 to 160 Hz depending on material composition and temperature. A general trend is that characteristic frequency increases with temperature. Resistance values vary from $0.0069 \Omega \text{ cm}^2$ at 850°C (for LSCNT-20) to $0.668 \Omega \text{ cm}^2$ at 700°C for LSCNT-10 (Fig. 28). This process's activation energies varied from 1.05 eV for LSCNT-5 to 2.2 eV for LSCNT-20 within 800 to 850°C temperature range (Fig. 29). These significant differences mentioned above conclude that the nature of this mid-frequency limiting process depends significantly on the electrode composition and temperature. The dependence of R_2 on p_{H_2} is also different in the case of different materials. In the case of LSCNT-5 R_2 decreases if hydrogen partial pressure p_{H_2} increases, but in the LSCNT-10, the R_2 increases with increased p_{H_2} (Fig. 30). As shown in the previous chapter, these characteristics indicate that these materials are very different and have a different response to the changes in p_{O_2} . Within this frequency range, the charge transfer limited step has been proposed in the literature [134,135]. However, there is only a minimal dependence of R_2 on the electrode polarization and very high thermal activation of the limiting process, so charge transfer limitation is rather unlikely in the materials studied in this case. Identification of limiting step needs additional systematic analysis.

The low-frequency semicircle ($-R_3\text{CPE}_3-$) appears in the case of all studied materials. The characteristic relaxation frequency varies from 0.4 to 1 Hz depending on temperature and material composition. Almost ideal capacitive behaviour appeared for all of the materials studied, judging from the exponent

values in CPE (0.94-1). The activation energies of the low-frequency process are highly dependent on the chemical stoichiometry of the material. Lowest $E_{a,R3}$ value was calculated for LSCNT-5, which was 0.83 eV. Similar $E_{a,R3}$ values for the LST-GDC system can be found from the literature [63]. The real part of the low-frequency semicircle (R_3) decreased if the electrode polarization decreased. R_3 was found to be also strongly dependent on p_{H_2} (Fig. 28 and Fig. 30). In literature, this water concentration-, temperature- and potential-dependent limitation process at low frequencies, approximately in the range from 0.1 to 1 Hz, has been attributed to the adsorption of hydrogen or reorganization of intermediates at electrode [63,135,136].

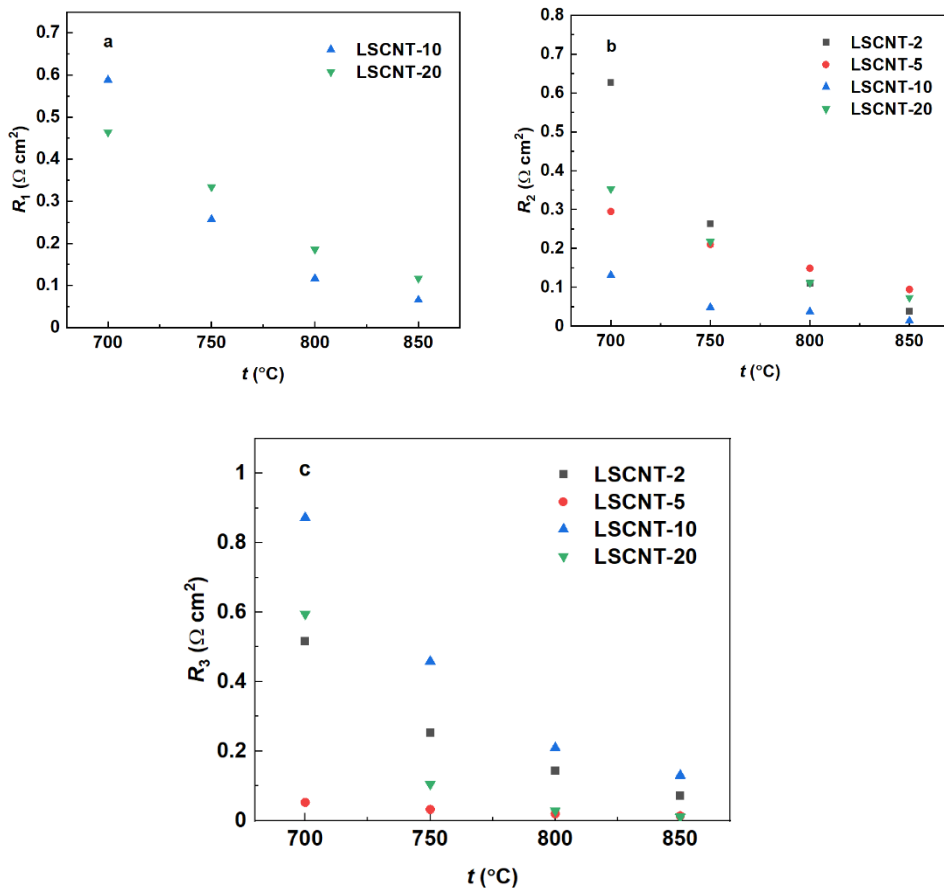


Figure 30. Temperature dependence of R_1 (a), R_2 (b) and R_3 (c) on for $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0.02, 0.05, 0.1$ or 0.2) electrode at 850 °C in humidified 50% H_2 , 50% Ar gas atmosphere measured at -0.9 V vs ref.

The R_s values measured for LSCNT-x electrodes at different temperatures are given in Fig. 28d. The LSCNT-5 has lower R_s values compared to values measured for all the other investigated electrodes. However, because absolute values of R_s were measured using the 3-electrode setup, these values depend on the exact position of the reference electrode and are not very well comparable. Thus, further comparative analysis based on R_s ' absolute values is given based on data collected using the 2-electrode measurement system given in the next section.

Table 4. Activation energies and characteristic frequencies for the limiting processes for $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0, 0.02, 0.05, 0.1$ or 0.2) electrodes at different Ni doping levels. Activation energies are calculated for limiting processes governing R_1 , R_2 and R_3 at working conditions (-0.9 V) and in the humidified H_2 . The activation energies were calculated in the range from 700 to 850 °C from Arrhenius plots.

	$E_{a,R1}$ (eV)	$f_{1 \text{ max}}$ (kHz)	$E_{a,R2}$ (eV)	$f_{2 \text{ max}}$ (Hz)	$E_{a,R3}$ (eV)	$f_{3 \text{ max}}$ (Hz)
LSCNT-2	-	-	1.18-1.7	25-150	1.31	0.5-1
LSCNT-5	-	-	1.05	37-60	0.83	0.4-0.5
LSCNT-10	1.22	4-6	1.11	25-60	1.13-2.5	0.4-0.8
LSCNT-20	1.28	6-23	1.18-2.2	32-160	1.01	0.37-0.95

LSCNT-5 has the lowest R_s and R_p values at all measured condition (Fig. 29 and Fig. 30). For example, at 850 °C and OCV conditions, the R_s was 0.25 and R_p 0.084 $\Omega \text{ cm}^2$, and at working conditions (-0.9 V) the R_s was 0.26 and R_p 0.065 $\Omega \text{ cm}^2$. At 700 °C, the R_p value for LSCNT-5 at operating conditions (-0.9 V) was 0.275 $\Omega \text{ cm}^2$.

LSCNT-5 was also the most stable of the measured electrode compositions. During the first 120 h of cell operation, the R_s of the electrode increased by approximately 2.2%, and R_p decreased by about 17.4%. Savaniu and Irvine [57] reported a similar decrease in R_p with $\text{La}_{0.9}\text{Sr}_{0.2}\text{TiO}_{3-\delta}$. In their case, the total resistance of the cell increased by about 20% during 12 h period after reduction at 600 °C. In our study, during 120-160 h, the degradation rate decreased to 0.2%/10 h for R_s . R_p values were stable and reached almost a plateau (0.22% decrease during 40 h).

6.3.3. Electrochemical characterization of $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ fuel electrode in 2-electrode button cell

To demonstrate the electrochemical performance of LSCNT-5 based electrode in operating SOFC conditions, electrochemical tests of SOFC button cell has been performed using 2-electrode configuration. In Fig. 31a, the Nyquist plots measured at OCV and operating conditions (-0.9 V) at two different temperatures (800 °C and 850 °C) as well as current- and power densities (b) of LSCNT-5(GDC)|GDC|ScCeSZ|GDC|LSC system are presented. From Nyquist plots, it can be observed that R_s values increase slightly if the potential is changed from OCV to operating conditions. This behaviour can be explained by the change of the impedance of fuel and air electrodes, resulting from a change in p_{O_2} in the porous electrodes. In the case of the fuel electrode, the increase of oxygen partial pressure during the cell polarization leads to a decrease of electronic conductivity of LSCNT-x according to equation 6 (given in literature overview paragraph) and a decrease in GDC conductivity [10], which both are responsible for the increase of R_s observed. It should be mentioned that the total conductance of the LSC cathode used in this single-cell increases very slightly with the increase of current density applied (explained by the decrease of p_{O_2} in the porous electrode). However, the conductance changes in the anode (decrease of conductance) are much more severe and define the total change in the system studied.

The change of R_p caused by cell potential also could be observed in Fig. 31a. The fuel electrode related mechanisms behind it are discussed in the previous chapter dealing with the 3-electrode characterization of LSCNT-x. In general, it should be noted that cathode impedance dominates in the Nyquist plots of the studied button cell at used experimental conditions.

It can be said that R_s ($0.63 \Omega \text{ cm}^2$ at 800 °C and OCV) values of the studied system are decent, and R_p values ($0.69 \Omega \text{ cm}^2$ at 800 °C and OCV) are excellent in comparison with the data presented in the literature for similar systems. For example, Lu et al. [62] demonstrated the R_p value of $1.86 \Omega \text{ cm}^2$ at 800 °C and OCV for undoped LSCT (YSZ electrolyte and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3/\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ cathode). They also demonstrated about 100 mW cm^{-2} power density for pure LSCT at -0.7 V cell potential otherwise at the same conditions. Our system containing LSCNT-5 material demonstrated 200 mW cm^{-2} (Fig. 31b) power density at similar conditions. The best power density (not peak power density) obtained in this study at 850 °C was 325 mW cm^{-2} . It could be concluded that optimal Ni-doping into the B-site of LSCNT leads to a significant increase in electrode activity.

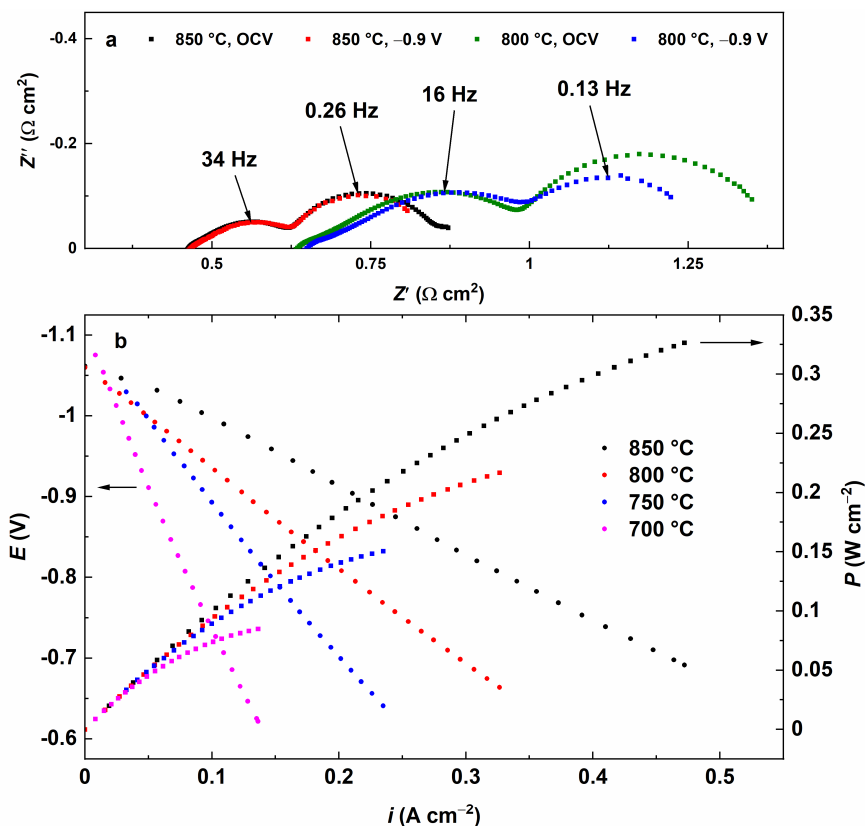


Figure 31. Nyquist plots (a) and cell potential vs current density and power density vs current density curves (b) measured in 97% H_2 , 3% H_2O atmosphere at different temperatures (700 °C, 750 °C, 800 °C and 850 °C) noted in the figure. Nyquist plots are measured at two different cell potentials (OCV and -0.9 V), and IE curves were recorded with a potential sweep rate of 5 mV s^{-1} .

7. SUMMARY

The main aim of this work was to develop an electrochemically active and stable solid oxide cell (SOC) fuel electrode. To rationally design the material, a more in-depth understanding between the crystallographic properties (lattice parameters, crystallite size, phase composition) of the SOC fuel electrode and its electrochemical performance and stability at operating conditions is necessary. A high-temperature *operando* XRD cell was developed and exploited to determine the crystallographic properties during cell operation conditions. Observing changes in these characteristics during the cell operation can help understand why some electrodes are underperforming.

The first part of the thesis focuses on testing the in-house developed *operando* XRD cell with Ni-GDC model fuel electrode. The test showed the capabilities of this method to obtain bulk crystallographic properties simultaneously with EIS data. Changes in GDC lattice parameter in different atmospheres (air, 1% H₂ in Ar and 5% H₂ in Ar) and during the electrode operation (−0.9 V vs Pt/Pt/O₂) were observed. The lattice expansion during electrode polarization is very significant and can be even equal to lattice expansion caused by a 50 °C increase in temperature. Another important aspect, which could be observed with the XRD coupled with EIS, was the changes in impedance at different times during NiO reduction reaction to Ni. Electrochemical properties remained constant after 60 mins of the reduction, although it took 160 minutes to reduce NiO entirely. Most likely, there are no significant changes in impedance after the exterior of NiO particles has been reduced to Ni. Therefore, as it was demonstrated, the reduction of NiO takes longer than could be presumed from impedance solely.

In the second part, extensive initial degradation of MIEC La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.3}Ni_{0.2}O_{3-δ} (LSCMN) electrode from LaCrO_{3-δ}-family were studied. The degradation was found to be partially reversible by conducting a redox cycle. The electrodes used in this were prepared by infiltrating LSCMN into a porous ScCeSZ electrolyte matrix. The formation of a new phase(s) during cell operation was observed on the surface of the fuel electrode. The particles were more prominent on electrodes operated in the electrolysis mode. The origin of the new phase was studied using the GIXRD technique at a LSCMN electrode deposited with pulsed laser deposition and likely was the Ruddlesden Popper ceramic phase of LSCMN. A high-temperature X-ray diffraction study (HT-XRD) was conducted at fuel cell *operando* conditions to understand the reason for the electrode degradation. The results show a significant reduction of the amount of LSCMN phase (~27 wt% less) with cell operation was observed simultaneously with an increase of the lattice parameter of the Sc_{0.2}Ce_{0.01}Zr_{0.79}O_{2-δ} (ScCeSZ) electrolyte. It is reasonable to conclude that some of the products of the LSCMN decomposition start to dope the ScCeSZ lattice, causing an increase in its lattice parameter. So, in the second part, it was

demonstrated that the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ electrode was not compatible with a $\text{Sc}_{0.2}\text{Ce}_{0.01}\text{Zr}_{0.79}\text{O}_{2-\delta}$ electrolyte.

In the third of these electrode from the $\text{SrTiO}_{3-\delta}$ perovskite family was studied. Influence of the Ni-doping level in $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0.02, 0.05, 0.1$ or 0.2) on the chemical composition of the surface, electrochemical characteristics, microstructural properties, microstructural response for redox cycle and on the short-term degradation was studied. 2-electrode measurements were conducted with the most active and stable material, $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (LSCNT-5) in order to evaluate the performance in real working conditions. The button cell consisted of LSCNT-5/GDC fuel electrode, two GDC barrier layers (between electrodes and electrolyte), ScCeSZ electrolyte and LSC air electrode. R_p value of $0.38 \Omega \text{ cm}^2$ at 850°C was observed, and power density of 325 mW cm^{-2} at 850°C (at -0.7 V cell potential) was measured.

The electrochemical performance of all the synthesized LSCNT- x electrodes was measured using a 3-electrode setup. The catalytically most active material was LSCNT-5, which had a polarization resistance value of $0.084 \Omega \text{ cm}^2$ at 850°C and OCV conditions. The polarization resistance was stable for 120 h, and no degradation was observed.

From the XRD analysis, it can be concluded that the unit cell volume of $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ (LSCNT- x) increases continuously with the Ni content in B-site. Starting from $x=0.1$ to higher concentrations of Ni in the LSCNT- x B-site NiO phase appears in diffractograms, i.e., LSCNT- x perovskite lattice is able to adopt less than 10% of Ni fully.

From the *in situ* XRD analysis of the powders, it can be said that during the first reduction cycle, irreversible changes take place in all studied LSCNT- x materials. The changes of unit cell volume as a response for changing the oxidizing atmosphere to reducing atmosphere are qualitatively different for non-doped $\text{La}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.4}\text{TiO}_{3-\delta}$ (LSCT), for 2% and 5% doped LSCNT- x and for compositions with Ni excess (10 and 20% of Ni). Moreover, the reversibility of the volumetric changes is dependent on the studied material – undoped LSCT undergoes more severe irreversible lattice deformation. These qualitative differences are also observable in electrochemical characteristics.

XPS and SEM analysis indicate some Ca segregation to the surface in the case of pure LSCT (without Ni-doping) in an oxidizing atmosphere. However, in reducing atmosphere, the material is stable and Ca stays in LSCT lattice. The analysis shows that CaO and other mobile A-site cation (Sr^{2+}) segregation can be suppressed in this material with Ni doping. The Ni content in B-site determines the surface chemistry and the proportion of La and Sr expressed on the surface. The TOF-SIMS data analysis confirms that the substitution of Ti with Ni in B-site leads to a more stable lattice and decreases the Sr mobility. However, in pure LSCT, there is the formation of a Sr-rich layer between electrolyte and a chemical barrier layer (accumulation of Sr and most likely formation of SrZrO_3) during the electrode sintering process. No formation of SrZrO_3 in Ni-doped materials has been observed.

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9. SUMMARY IN ESTONIAN

Keraamilise kütuseelektroodi arendamine tahkeoksiidelemendile

Töö eesmärk oli arendada elektrokeemiliselt aktiivne ning stabiilne kütuseelektrood tahkeoksiidelemendile. Selleks, et jälgida materjali ülesehituses toimuvaid muutusi kütuseelemendi töötamisega samaaegselt, koostati uudne kõrgtemperatuurine *operando* röntgendifraktsiooni (XRD) mõõterakk. See mõõterakk võimaldas saada infot korraga nii kütuseelemendi elektroodi elektrokeemiliste kui ka kristallograafiliste omaduste (võreparameeter, kristalliidi suurus, faasiline koostis) kohta. Nii oli võimalik analüüsida, kuidas mõjutavad muutused elektroodi struktuuris kütuseelemendi elektrokeemilist toimimist ning mõista paremini elektroodides toimuvaid protsesse.

Uudse *operando* XRD mõõtesüsteemiga uuriti Ni-GDC mudelelektroodis toimuvaid protsesse. Mudelelektroodil lasti töödada erinevates gaasikeskkondades ja erineva elektrokeemilise polarisatsiooniga ning hinnati sellele vastavaid kristallifaaside võreparameetrite muutuseid. Leiti, et sõltuvalt voolutihedusest muutus $\text{Ce}_{0,9}\text{Gd}_{0,1}\text{O}_{2-\delta}$ (GDC) võreparameeter märkimisväärselt. Ühikraku suuruse muutused elektroodi polarisatsiooni muutmisel avatud ahela potentsiaal (OCV) kuni $-0,9\text{ V}$ -ni on võrreldavad võre paisumisega, mis kaasneb $50\text{ }^{\circ}\text{C}$ temperatuuri tõusuga. Võre järsk paisumine tekitab aga pingeid elektroodi elektrolüüdi piirpinnal, mis võib kütuseelemendi lõhkuda. Seega oleks mõistlik polarisatsiooni muuta järk-järgult. Teine oluline protsess, mida nähti, oli NiO redutseerumine niklik. See muutis korraga nii elektroodi impedantsi kui ka kristallifaasi parameetreid. Pärast 60. minutit NiO redutseerumist jäid elektrokeemilised omadused muutumatuks, aga nikkeloksiidi täielikuks redutseerimiseks kulus 160 minutit. Sellest järeldub, et suure tõenäosusega jääb elektroodi impedants peaaegu konstantseks juba pärast NiO osakeste pinna redutseerumist niklik, kuigi osakeste täieliku redutseerumiseni kulub veel pikk aeg.

Veel uuriti, mis põhjustab $\text{La}_{0,75}\text{Sr}_{0,25}\text{Cr}_{0,5}\text{Mn}_{0,3}\text{Ni}_{0,2}\text{O}_{3-\delta}$ (LSCMN) kütuseelektroodi intensiivset degradeerumist esialgses stabiliseerumise faasis. Kütuseelektrood valmistamiseks infiltreeriti aktiivaine (LSCMN) poorsesse $\text{Sc}_{0,2}\text{Ce}_{0,01}\text{Zr}_{0,79}\text{O}_{2-\delta}$ (ScCeSZ) elektrolüüdi maatriksisse. Töötingimuste mõju materjali pinnastruktuurile uuriti GI-XRD ning SEM meetoditega. Selgus, et elektroodi töö käigus tekkis selle pinnale uus kristallifaas, mis suure tõenäosusega kuulus LSCMN-i Ruddlesdeni-Popperi faasile. Lisaks uuriti elektroodi degradeerumise põhjuseid *operando* XRD meetodiga. Avastati, et katse käigus vähenes LSCMN-i faasi hulk ~ 27 massi%, kusjuures ScCeSZ võreparameeter kasvas elektroodi töötingimustel järk-järgult. Suure tõenäosusega põhjustab ScCeSZ võreparameetri kasvu selle ühikraku elementkoostise muutumine, mis juhtub arvatavasti seetõttu, et mõni LSCMN-i lagunemise produktidest dopeerib ScCeSZ võre.

Doktoritöö käigus uuriti veel $\text{SrTiO}_{3-\delta}$ perovskiidi tüüpi segajuhtmaterjale $\text{La}_{0,25}\text{Sr}_{0,25}\text{Ca}_{0,4}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ (LSCNT-x), kus x on 0,02, 0,05, 0,1 või 0,2. Hinnati Ni hulga mõju elektroodi pinnakeemiale, elektrokeemilistele omadustele, mikrostruktuurile, redokstsüklile ning lühiajalisele stabiilsusele. Kõige aktiivsemat materjali, $\text{La}_{0,25}\text{Sr}_{0,25}\text{Ca}_{0,4}\text{Ti}_{0,95}\text{Ni}_{0,05}\text{O}_{3-\delta}$ (LSCNT-5), mõõdeti 2-elektroodse süsteemiga, et hinnata elektroodi aktiivsust tahkeoksiidses elektrokeemilises rakus. See elektrokeemiline rakk koosnes LSCNT-5/GDC kütuse-elektroodist, kahest GDC barjäärkihist (elektroodide ja elektrolüüdi vahel), ScCeSZ elektrolüüdist ning $\text{La}_{0,6}\text{Sr}_{0,4}\text{CoO}_{3-\delta}$ õhuelektroodist. Polariseerimise (R_p) väärtuseks mõõdeti 850 °C juures 0,38 $\Omega \text{ cm}^2$ ning võimsustiheduseks 325 mW cm^{-2} (-0,7 V rakupotentsiaal).

Kõikide sünteesitud LSCNT-x elektroodide elektrokeemilist aktiivsust hinnati ka 3-elektroodses süsteemis. Kõige aktiivsema materjali (LSCNT-5) R_p väärtus oli 850 °C juures ning avatud ahela potentsiaalil 0,084 $\Omega \text{ cm}^2$. Leiti, et R_p oli stabiilne kogu esialgse stabiilsuskatse vältel, mis kestis 120 h.

XRD analüüsist järeldub, et nikli kontsentratsiooni kasv LSCNT-x võres suurendab faasi ühikraku ruumala. Samas, alates $x = 0,1$ ei lahustu nikkel enam täielikult LSCNT-x võres ja osa Ni moodustab NiO faasi.

In situ XRD analüüsiga uuriti elektroodimaterjali stabiilsust redokstsüklite suhtes. Esimese redutseerimise tagajärjel suurenes kõikides LSCNT-x pulbrites pöördumatult ühikraku ruumala. Need muutused olid erinevad olenevalt materjali koostisest. Tekkis kolm gruppi: puhas $\text{La}_{0,25}\text{Sr}_{0,25}\text{Ca}_{0,4}\text{TiO}_{3-\delta}$ (LSCT), 2% ning 5% niklisisaldusega (B-saidis) LSCNT-x ning nikli liiaga materjali (10 ja 20% niklit B-saidis LSCNT-x). Samad kolm gruppi moodustusid ka elektrokeemiliste tulemuste põhjal. *In situ* XRD meetodiga selgus veel, et osade materjalide võre ruumala muutus redutseerimise tagajärjel rohkem pöördumatult, osadel rohkem pöördumatult. Näiteks dopeerimata LSCT materjalis deformeerub võre intensiivselt ja suures osas pöördumatult.

XPS ja SEM analüüsist johtub, et Ca^{2+} ioonid liiguvad puhtas LSCT-s (õhu keskkonnas ning elektroodi töötemperatuuril) pinnale. Samas redutseerivas keskkonnas Ca^{2+} -ioonid pinnale ei liigu, vaid jäävad LSCT võresse. Analüüsist järeldus veel, et dopeerimine nikliga vähendas märgatavalt A-saidi katioonide mobiilsust LSCNT-x elektroodis. Nikli kontsentratsioon LSCNT-x B-saidis mõjutas otseselt $\text{La}^{3+}/\text{Sr}^{2+}$ kontsentratsioonide suhet elektroodi pinnal. TOF-SIMS analüüs kinnitas samuti, et nikli lisand LSCNT-x võres parandas selle stabiilsust ning vähendas strontsiumi mobiilsust. TOF-SIMS kujutistel oli näha puhta LSCT elektroodi ning ScCeSZ elektrolüüdi vahele kogunenud Sr-rikas kiht. Samas kui kõikide nikliga dopeeritud materjalide korral leidis Sr ainult elektroodikihis.

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2014–2016 Skeleton Technologies OÜ, Sünteesioperaator

Teaduspublikatsioonid:

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