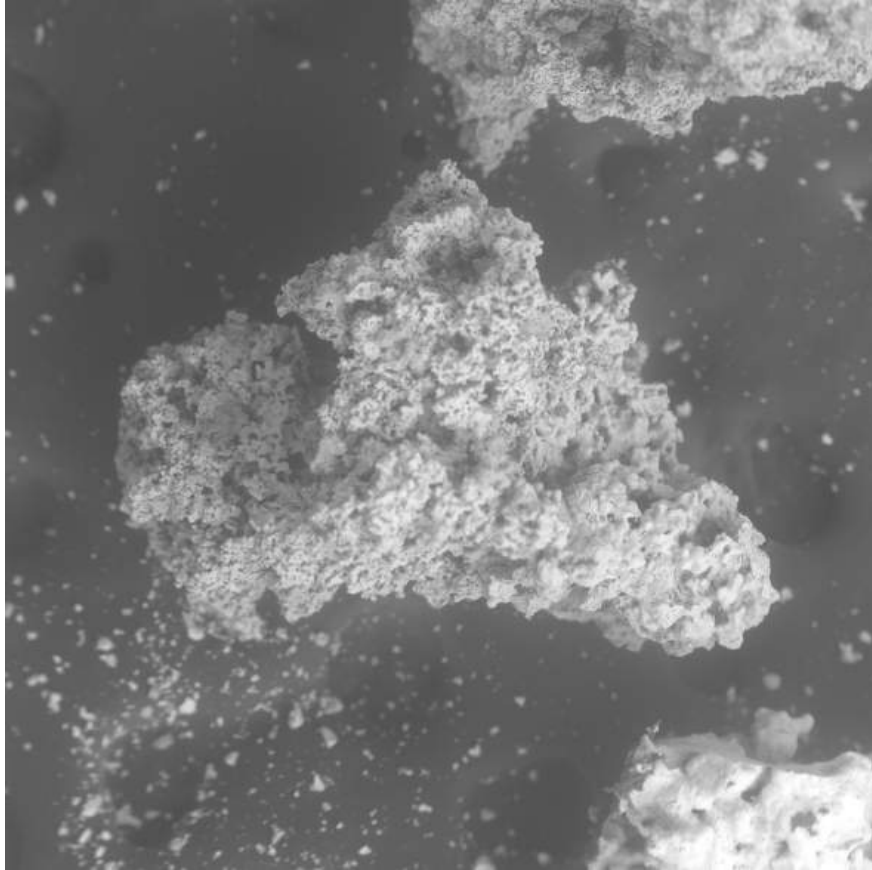




CHALMERS
UNIVERSITY OF TECHNOLOGY



Perovskite Materials for Hydrogen Production

Synthesis and Evaluation of Perovskite Metal Oxides for Hydrogen Production Using Chemical Looping Water Splitting

Master's thesis in Innovative and Sustainable Chemical Engineering

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DEPARTMENT OF ENVIRONMENTAL AND ENERGY SCIENCES

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2026

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MASTER'S THESIS 2026

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ALEXANDER KLUTE

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Cover: Micrograph of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle.

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Abstract

In order for hydrogen production to become more sustainable, other types of green hydrogen production apart from electrolysis need to be developed due to electrolysis's high cost. Chemical Looping Water Splitting, utilising the steam-iron reaction in fluidised bed reactors, is one such method. Poor kinetics and mechanical integrity of iron oxide means that other types of metal oxides need to be developed for use instead. The aim of the thesis was to synthesise different perovskite metal oxides to be used in a CLWS system and test them in small-scale batch fluidised bed reactors. The aim of the batch experiments was to determine the hydrogen production capacity, hydrogen production rate and find the optimum temperature of the steam reactor. Changes to the particles morphology was also analysed using SEM. Four different types of metal oxides with perovskite structure were successfully synthesised using solid-state synthesis, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$. The perovskite structure was verified using powder XRD. $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ were unsuitable for CLWS due to being unable to be fluidised. $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ was unsuitable for CLWS due to defluidisation of the reactor occurring, limiting HPC and HPR. The HPR at 900°C was 0.1458 mmol g⁻¹ and the HPR at the same temperature was 0.051 mmol g⁻¹ min⁻¹. $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ did not defluidise but was very limited by its thermodynamic properties. The maximum HPC was achieved at 800°C and the maximum HPR was achieved at 850°C. The HPC at 800°C was 0.179 mmol g⁻¹ and the HPR at 850°C was 0.042 mmol g⁻¹ min⁻¹. The performance of both $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ decreased with each successive cycle. The performance of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ was mainly affected by defluidisation of the reactor with the CO conversion decreasing at smaller δ_{FR} values after defluidisation. The performance of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ was mainly affected by undergoing 46 cycles, with the conversion decreasing at smaller δ_{FR} values every cycle. The morphology changes to the $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particles were significant due to defluidisation. The surfaces of the particles became smoother. The morphology changes to the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles occurred due to repeated use and they became more porous and fragmented but otherwise remained largely intact.

Keywords: Chemical Looping, Chemical Looping Water Splitting, Perovskite, Hydrogen production, Oxygen carriers, Steam-Iron process, Fluidised Bed Reactor.

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First of all I would like to thank my project supervisor Ivana Staničić and my examiner Magnus Rydén. Their help and feedback have been invaluable during this project, especially when it looked like only one of the particles was able to be fluidised. I would would also like to thank Hai Co Nguyen for all the help in the lab when things weren't working as they should.

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Alexander Klute, Gothenburg, June 2026

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

AR	Air Reactor
CLWS	Chemical Looping Water Splitting
FBR	Fluidised Bed Reactor
FR	Fuel Reactor
OC	Oxygen Carrier
PVA	Polyvinyl Alcohol
SEM-EDS	Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy
SR	Steam Reactor
XRD	X-ray Diffraction

Nomenclature

Below is the nomenclature of the variables that have been used throughout this thesis.

Variables

f	Goldschmidt tolerance factor	[-]
HPC	Hydrogen production capacity	[mmol g ⁻¹]
$\overline{HPC}$	Mean hydrogen production capacity	[mmol g ⁻¹]
HPR	Hydrogen production rate	[mmol g ⁻¹ min ⁻¹]
$\overline{HPR}$	Mean hydrogen production rate	[mmol g ⁻¹ min ⁻¹]
M	Molar mass	[g mol ⁻¹]
m	Mass of particles	[g]
Δm_{OC}	Oxygen carrier mass loss	[g]
P	Pressure	[Pa]
ΔP	Pressure drop	[kPa]
$\frac{d\Delta P}{dt}$	Gradient of the pressure drop	[kPa s ⁻¹]
R	Ideal gas constant	[J K ⁻¹ mol ⁻¹]
r	Ionic radius	[Å]
t	Time	[s]
T	Temperature	[K]
$\dot{V}$	Volumetric flow rate	[mL min ⁻¹]
x	Gas concentration	[-]
Y	Mass yield of particle synthesis	[%]
γ_{CO}	Gas conversion of carbon monoxide in fuel reactor	[-]
δ	Oxygen deficiency	[-]
$\frac{d\delta}{dt}$	Reaction rate, δ basis	[s ⁻¹]

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1

Introduction

1.1 Background

According to the International Panel on Climate Change, hydrogen is an important energy carrier in many industries if decarbonisation is to be achieved, such as steel making and chemical production, due to the absence of carbon dioxide produced when consumed [1]. However, less than 1% of total global hydrogen production in 2025 was produced with low CO₂ emission methods [2].

The most common method of producing hydrogen today is steam methane reforming where methane reacts with steam to form hydrogen gas and carbon dioxide [3]. This reaction is strongly exothermic which leads to high energy costs which further increases carbon dioxide emissions. The methane used comes from natural gas. Hydrogen produced from natural gas is known as grey hydrogen. Grey hydrogen directly connected to carbon capture is known as blue hydrogen. If hydrogen is to be used as a sustainable fuel source other methods need to be used with low carbon dioxide emissions also known as green hydrogen.

The main low emission hydrogen production method used today is electrolysis [4]. This method is promising but it has problems with scalability and high energy costs which makes it difficult and expensive to implement on the large scale needed. It is also highly dependent on low cost renewable electricity to drive the process. If low emission hydrogen production is to meet the increasing demands for energy carriers with low CO₂ emissions, then other methods need to be developed.

One of the oldest methods for hydrogen production is the steam-iron process [5]. This process was non-continuous, and it worked by oxidising Fe₃O₄ with air to form Fe₂O₃, then reducing Fe₂O₃ using gasified coal to FeO. FeO is then oxidised back to Fe₃O₄ using steam which produced hydrogen gas. The process is then repeated. The steam iron process was eventually out-competed by processes such as steam methane reforming mentioned earlier [3].

Chemical Looping Water Splitting (CLWS) is a continuous version of the steam-iron process using three fluidised bed reactors (FBR:s) where the three steps in the steam-iron process occur in the different reactors [6]. If biogas is used as fuel, green hydrogen can be produced using this method. Blue hydrogen can also be produced if fossil fuels are used instead. The iron oxide particles act as oxygen carriers (OC:s)

that transport oxygen between the reactors. This enables the three reaction steps to be easily performed at different temperatures. The use of fluidised bed reactors also improves heat and mass transfer between the gas and iron oxide which improves kinetics. Due to the air oxidation and fuel reduction happening in separate reactors the CO_2 is easily separated for carbon capture.

CLWS using iron oxide has its own disadvantages [7]. When the iron oxide is reduced too far the particles can sinter and agglomerate causing defluidisation of the reactor. The steam conversion is limited by the oxidation states of iron oxide. Additionally, the kinetics of the steam reactor and fuel reactor are slow. For this reason, other types of oxygen carriers are of interest. However, the number of choices for conventional known oxides is very small. Of the common monometallic oxides, iron oxide is the only one possible. The reason for this is that many metal oxides are locked to a few oxidation numbers and the thermodynamics simply don't allow for large amounts of hydrogen to be produced. For this reason more complex mixed metal oxides are of interest to replace iron oxide.

Perovskite metal oxides with the structure $\text{ABO}_{3-\delta}$ are one such example of complex metal oxides with the potential for use in CLWS [8]. A and B are cations of different sizes and allow for customisation of the chemical structure of the metal oxides. A and B are also not limited to one type of cation. There could be multiple types of cations at the A site and B site. This leads to there being practically infinitely many combinations of A and B, which allows for the tuning of the perovskite metal oxide to have the desired chemical properties.

1.2 Aim

The aim of this master's thesis is to synthesise several perovskite metal oxide oxygen carriers to be used in a chemical looping water splitting system, analyse their composition and evaluate the hydrogen production potential and hydrogen production rate in a small-scale batch CLWS system.

1.2.1 Limitations

The project will focus on the synthesis, analysis and hydrogen production potential of the perovskite metal oxides. No techno-economic analysis will be performed, and no sustainability analysis of the perovskites will be performed.

1.2.2 Objectives

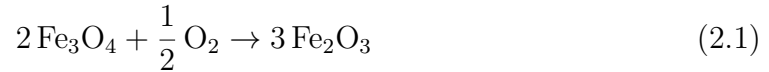
- Determine the hydrogen production capacity and hydrogen production rate of the selected perovskite metal oxide oxygen carriers.
- Determine the optimal temperature for hydrogen production capacity and hydrogen production rate.
- Examine how the particles' morphology and performance are affected by undergoing many cycles of air oxidation, fuel reduction and steam oxidation.

2

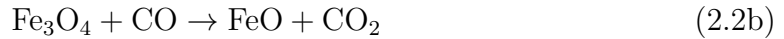
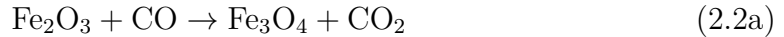
Theory

2.1 Steam-Iron Process

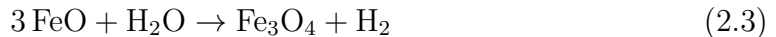
As previously mentioned, the steam iron process is an old method for producing hydrogen that has been outcompeted by other, cheaper methods. The steam-iron process consists of three redox reaction steps. The first step is the complete oxidation of iron oxide with air [5]. This oxidation reaction is shown in equation 2.1.



The second step is reducing Fe_2O_3 with some sort of fuel [5]. This reduction reaction, using CO as fuel, happens in multiple steps and is shown in equations 2.2a and 2.2b.



After reduction with fuel the FeO is then oxidised using steam to produce hydrogen. This oxidation reaction is shown in equation 2.3.



Reaction 2.3 is exothermic and entropy-decreasing, causing the equilibrium steam conversion to decrease with increasing temperature [7]. However, the reaction kinetics improve at higher temperatures, resulting in an optimum temperature for maximum steam conversion. For iron oxide, this optimum occurs at 800°C. Reactions 2.1 and 2.2a exhibit the same exothermic and entropy-decreasing behaviour. In contrast, Reaction 2.2b is endothermic and entropy-increasing, resulting in increased reactivity and CO conversion at higher temperatures.

2.2 Fluidised Bed Reactors

Fluidised bed reactors (FBR:s) are heterogenous reactors consisting of solid particles and an upwards flow of fluid, liquid or gas [9]. When a bed of solid particles is exposed to a flow of fluid from below, a drag force is applied on the particles by the fluid. When the fluid velocity is large enough, the drag force of the fluid counteracts gravity and the bed transitions from a fixed bed, where the particles are stationary, to a fluidised bed, where the particles are moved around by the gas, with similar behaviour to a fluid. Due to the fluid-like behaviour, the heat and mass transfer coefficients between the fluid and particles increase significantly and the mixing of the solid particles that occurs leads to a more uniform temperature distribution in the bed. The pressure drop over the reactor and flow rate through the reactor have large fluctuations. Attrition of the solid particles can occur which leads to worse reactor performance over time. Particle agglomeration can also occur which can cause defluidisation of the bed, severely compromising reactor operation. Defluidisation prevents particle transfer between reactors, significantly reduces reaction kinetics, and may require reactor shutdown to remove the agglomerates. Therefore, avoiding defluidisation is essential for stable reactor operation.

The particles can also agglomerate which causes the bed to undergo defluidisation, which has catastrophic consequences for the reactor. The particles are unable to be moved between reactors, the kinetics are significantly reduced and the reactor needs to be shutdown so that the agglomerates can be removed. This means that defluidisation should be avoided at all costs.

Particle agglomeration can cause bed defluidisation, severely compromising reactor operation. Defluidisation prevents particle transfer between reactors, significantly reduces reaction kinetics, and requires reactor shutdown to remove the agglomerates. Therefore, preventing defluidisation is essential for stable reactor operation.

There exist many different industrial applications of FBR:s, including in the chemical and energy industries [10]. The solid particles are used as catalysts for chemical reactions and as reactants in chemical reactions. Applications in the chemical industry include fluidised catalytic cracking, which converts high molecular weight hydrocarbons into petrol, alkenes and other petroleum products. Another application is in the production of acrylonitrile. Applications in the energy industry include bubbling fluidised bed boilers and circulating fluidised bed boilers.

2.3 Chemical Looping Water Splitting

A continuous version of the steam-iron process using fluidised bed reactors is known as Chemical Looping Water Splitting (CLWS), where the steam-iron process is made continuous using fluidised bed reactors where gas is bubbled through a bed of iron oxide particles [7]. The iron oxide particles act as oxygen carriers (OC:s), where oxygen is transported between the reactors using the iron oxide particles. The CLWS process is described in figure 2.1. In the air reactor (AR), reaction 2.1 occurs

where Fe_3O_4 is oxidised to Fe_2O_3 , producing heat. In the fuel reactor (FR), reactions 2.2a and 2.2b occur, reducing Fe_2O_3 to FeO . Then the FeO is transported to the steam reactor (SR) where reaction 2.3 occurs, partially oxidising the FeO to Fe_3O_4 , producing hydrogen. Due to the air and fuel not mixing, this process allows for hydrogen production with intrinsic CO_2 capture. When iron oxide is reduced too far and Fe starts forming, sintering of the oxygen carrier particles can occur which leads to agglomeration of the particles and defluidisation of the bed occurs. This limits the FR to reaction 2.2b which in turn limits the SR to reaction 2.3.

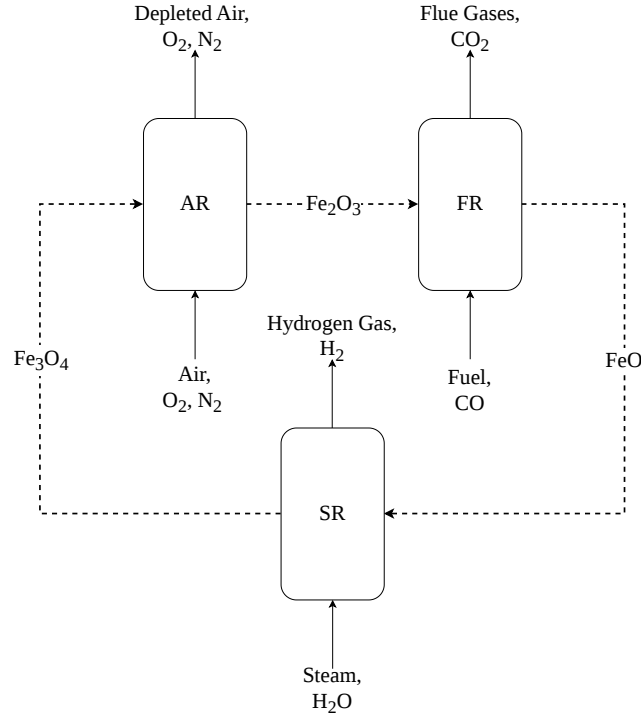


Figure 2.1: Chemical looping water splitting with iron oxide(Fe_2O_3) as the oxygen carrier and CO as fuel.

2.4 Perovskite Metal Oxides

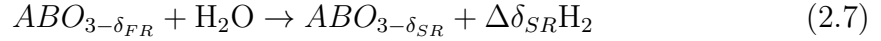
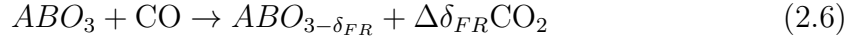
Perovskite metal oxides are a category of metal oxides with a specific chemical structure, $\text{ABO}_{3-\delta}$ [11]. A and B are cations of different sizes with the A site cation typically being the larger cation. Most synthesised perovskites are chosen to have rare-earth metals or alkaline earth metals at the A site and transition metals such as Fe, Co and Mn at the B site. The perovskite metal oxides are not restricted to only having one type of cation on the A or B site, allowing for practically infinite combinations. This then allows the chemical properties of the perovskite metal oxides to be tuned by substituting different cations on the A and B sites. The δ value describes the oxygen deficiency of the perovskite metal oxide and is the molar ratio between the amount of oxygen that has left the metal oxide and the total amount of metal oxide.

The crystal structure of the perovskite metal oxide depends on the ionic radii of the cations on the A and B sites [12]. The crystal structure can be predicted using the Goldschmidt tolerance factor, f . The Goldschmidt tolerance factor is calculated using equation 2.4.

$$f = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (2.4)$$

r_A is the ionic radius of the A site cation, r_B is the ionic radius of the B site cation and r_O is the ionic radius of oxygen. An f value of 1 represents an ideal perovskite with a cubic crystal structure, however this is rarely the case and different values of f are usually obtained for perovskite metal oxides. In general, when f is between 0.9 - 1.0 the perovskite have a cubic structure, between 0.71-0.9 the crystal structure distorts to an orthorhombic or rhombohedral crystal structure[13]. When f is below 0.71 or above 1, perovskite structure is typically not formed. These rules are not strict and deviations from these rules are common.

Substituting $ABO_{3-\delta}$ into equations 2.1, 2.2 and 2.3 gives equations 2.5, 2.6 and 2.7. that when using a perovskite metal oxide as the oxygen carrier for CLWS gives the reactions for the AR, FR and SR respectively.



δ_{FR} is the oxygen deficiency in the FR and δ_{SR} is the oxygen deficiency in the SR.

The typical maximum allowed δ value is 0.5 [14]. This is because when the perovskite structure is reduced this far, structural decomposition can occur and the perovskite metal oxide becomes a brownmillerite metal oxide with the general structure $A_2B_2O_5$.

3

Methods

In figure 3.1 an overview of the workflow of the project can be seen. First four different perovskite metal oxides were chosen to be synthesised. Small batches of these were then synthesised and analysed using powder XRD to verify that perovskite structure had been formed. After this, large batches were synthesised to be used in CLWS experiments. If the particles did not fluidise then the calcination temperature during synthesis was increased. If the particles still did not fluidise, they were rejected and no CLWS experiments were performed. SEM micrographs were taken for all particles, used and unused.

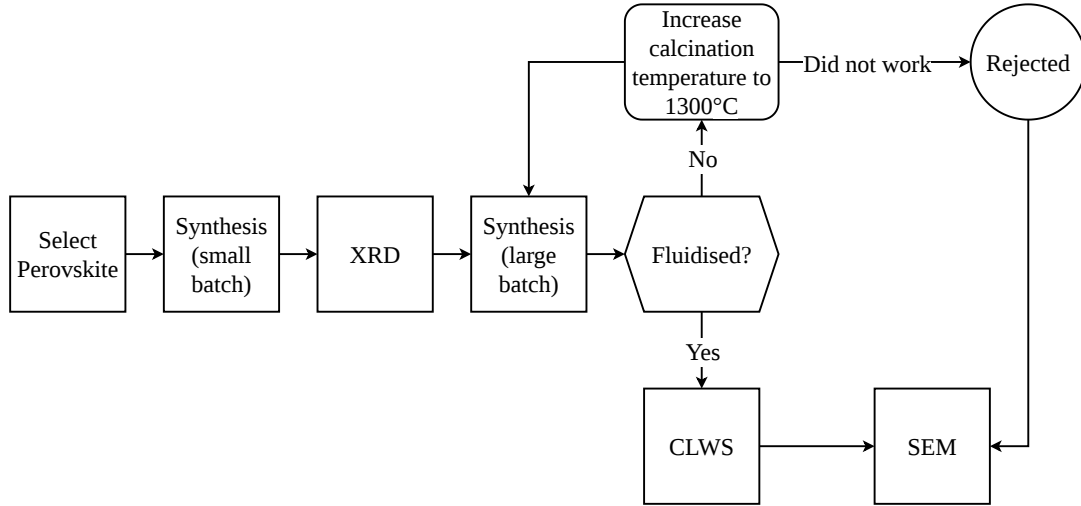


Figure 3.1: Workflow of project including synthesis, analysis and selection of particles to be used in CLWS experiments.

Four different perovskite metal oxides were chosen to be synthesised.

$\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$. $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ was chosen based on previous research by Àlex Fuentes Ruiz [15]. In this study several perovskite metal oxides based on Ca and La on the A site and Fe and Mn on the B site were investigated and $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_3$ was found to be the most appropriate oxygen carrier for CLWS. $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ were chosen based on findings from a machine learning model by Brorsson et al [16]. The Goldschmidt tolerance factors for all four OC:s can be seen in table 3.1. The ionic radii used for the Goldschmidt tolerance factor calculations were taken from the revised

effective ionic radii by Shannon [17].

Table 3.1: Goldschmidt tolerance factor, f , and predicted crystal structure for $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$.

OC	f	Predicted crystal structure
$\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$	0.951	cubic
$\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$	0.923	cubic
$\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$	0.955	cubic
$\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$	0.955	cubic

The experimental part was divided into three different parts: synthesis, analysis and batch fluidised bed experiments. In the synthesis section, the synthesis method is described. In the analysis section, the analytical methods used to analyse the particles' structure, density and morphology are described. The analysis of the particles' morphology was performed before and after the CLWS experiments. In the batch fluidised bed experiments section, experiments were performed in a small scale batch reactor in order to simulate a CLWS system.

3.1 Perovskite Synthesis

At first, 5g samples of the different metal oxides were synthesised and then analysed using XRD. After XRD analysis, larger batches of the different perovskites were synthesised. The perovskites were synthesised by mixing basic metal oxides containing the metals required to form the desired particles and then mixing a few drops of 10% polyvinyl alcohol (PVA) solution as a binder before calcination in a high temperature oven. Two 5 g samples of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ were synthesised, one with a 2-3 drops of the PVA solution so that the texture of the mixture was like wet soil and one with 2 more drops so that the texture was like clay. In table 3.2 the amounts of basic metal oxides used to synthesise 5g batches of the different perovskites.

Table 3.2: Metal oxide masses in grams used for the synthesis of 5 g samples of the different perovskite metal oxides.

Oxide	$\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$	$\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$	$\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$	$\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$
MgO [g]	0	0.55	0	0.079
CaO [g]	0.70	0	0.96	0.99
Y ₂ O ₃ [g]	0	0	1.50	1.32
La ₂ O ₃ [g]	2.10	2.21	0	0
Mn ₂ O ₃ [g]	0	2.14	2.40	2.46
Fe ₂ O ₃ [g]	2.10	0	0	0

After homogenisation with PVA the mixtures were put in ceramic boat which were then put in a high temperature oven for calcination. In figure 3.2 the metal oxide mixtures in the ceramic boats can be seen.



Figure 3.2: 5g samples of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ before calcination. From left to right: $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$.

Calcination was performed for two reasons. Firstly, synthesising the perovskites and secondly, to increase the density of the particles. In table 3.3 the oven program is shown. After calcination, the particles were gently crushed and sieved to the selected size distribution, between $90\text{ }\mu\text{m}$ and $180\text{ }\mu\text{m}$.

Table 3.3: Temperature program of oven used for calcination of the perovskite metal oxides.

Temperature [$^{\circ}\text{C}$]	Time [min]	Type
25 $\rightarrow$ 300	60	rate
300	60	dwell
300 $\rightarrow$ 800	100	rate
800	120	dwell
800 $\rightarrow$ 1250/1300	90	rate
1250/1300	540	dwell
1250 $\rightarrow$ 25	49	rate

A 30 g batch of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ was then synthesised using the same mass ratios as in table 3.2. 40 g batches of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ were synthesised. The large batches were then also sieved to the selected size distribution. The mass yield was calculated as the mass ratio between the mass of the particles in the selected size range and the total mass of the metal oxides used for synthesis. This was calculated using Equation 3.1.

$$Y = \frac{m_{90\mu\text{m}-180\mu\text{m}}}{m_{\text{ox}}} \times 100\% \quad (3.1)$$

3.2 Particle Analysis

The particles were analysed using three different methods. First, the crystal structure was analysed using powder X-ray diffraction in order to determine if perovskite structure had been formed. They were then analysed using SEM to determine the particles morphology and the bulk density was also measured. These analyses were performed to determine the suitability of the particles for use in the CLWS experiments. SEM-EDS was repeated after the CLWS experiments in order to compare the particles morphology before and after undergoing the CLWS experiments.

3.2.1 Powder X-ray Diffraction

Powder X-ray diffraction, XRD, is an analytical tool that can be used to determine the crystal structure of solid phase materials [18]. It works by subjecting a powdered sample with an x-ray beam of a certain wavelength at different angles and then measuring the scattered x-ray waves. The intensity of the measured scattered X-ray waves is then plotted as a function of the angle in a diffractogram. At some angles the scattered X-ray waves constructively interfere which causes intensity peaks in the diffractogram. Different crystal structures cause constructive interference to occur at different angles, which enables characterisation of the crystal structure. Different atoms within the same crystal structure also cause constructive interference to occur at different angles, although this effect is small in comparison which makes identifying specific atomic structures very difficult.

The X-ray diffraction analysis was performed using a BRUKER D8 Discover all-purpose X-ray diffractometer equipped with Cu radiation ($\lambda = 1.58 \text{ \AA}$) operated at 40 kV and 40 mA. The measurements were carried out between 10° and 90° with a step size of $0.03^\circ \text{ s}^{-1}$. The diffractograms were visualised with the DIFFRAC.EVA software and then compared with reference data from the Crystallography Open Database and PDF5+ 2025 database to determine the crystal structure(s) present in the samples.

3.2.2 SEM-EDS

Scanning Electron Microscopy Energy-Dispersive X-ray Spectroscopy, SEM-EDS, is an analytical tool used for two different purposes [19]. The Scanning Electron Microscopy (SEM) is similar to a conventional optical microscope but instead of using light to visualise a small sample, it uses electrons. It works by subjecting a sample to an electron beam. When the electrons from the electron beam interact elastically with the sample, backscattering of the beam electrons occurs which when measured allows for high resolution images of a sample. This allows for much higher resolution compared to optical microscopes which enables the visualisation of much smaller samples. The downside is, however, that colour cannot be detected with SEM. When an electron from the electron beam displaces an electron from an inner shell of an atom, an electron from an outer shell takes its place which causes the electron from the outer shell to lose energy in the form of an X-ray photon. The

energies of these photons are different for each element which allows for characterisation of a sample.

The SEM-EDS analysis was carried out using a Phenom Pure G7 Desktop SEM with an installed EDS detector. Micrographs were taken at different resolutions to examine the particles' morphology using back-scattered electrons. EDS measurements were also performed on $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ to examine the atomic concentration of metal atoms in different places on the particles.

3.2.3 Bulk density

The bulk density measurements were performed in accordance with standard ISO 3923-1:2008. The particles were poured into a funnel with a 2.5 mm orifice where the particles could flow into a cylindrical cup with a volume of 9.9 cm³. The particles were then levelled. The cup was gently tapped and to settle the particles and then the cup containing the powder was weighed. This was then repeated two more times for a total of three times and the mean value was calculated.

3.3 CLWS Experiments

Chemical looping water splitting experiments were performed using two of the synthesised oxygen carriers, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$. The other two oxygen carriers, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$, could not be fluidised and experiments were therefore not performed.

3.3.1 Experimental Setup

The chemical looping water splitting system was simulated using a fluidised bed batch reactor where the gas flow composition into the reactor was changed to simulate the air reactor, fuel reactor and steam reactor. In between each reactor phase an inert gas, N_2 , was used to clear the reactor of previous gases to ensure they don't interfere with the next reactor phase. The oxidation phase was performed until the O_2 gas concentration reached its maximum and the SR phase was performed until the H_2 gas concentration reached below 0.1 %. When the SR phase was performed at a different temperature to the FR phase and AR phase, the oven temperature was changed during the intermittent inert phase and the reactor temperature was allowed to settle during the inert phase. In table 3.4 the gas composition and flow rates of the different phases are shown. Note that the flow rates are for the gas flows at the magnetic vents where the temperature is assumed to be 25 °C and the pressure 1 atm.

3. Methods

Table 3.4: Gas composition and flow rates for the different phases.

Phase	Gases	Flow Rate [mL min ⁻¹]	Temperature [°C]
Oxidation (AR)	Synthetic air	250	900
	N ₂	750	
Inert	N ₂	1000	900
	CO	450	
Reduction (FR)	N ₂	550	900
	N ₂	1000	
Steam (SR)	Steam	600	700 - 900
	N ₂	500	
Inert	N ₂	1000	900

The CLWS experiments were performed in a fluidised bed batch reactor made of quartz. The oxygen carrier particles were inserted inside the reactor where a porous plate held them in place while still allowing gas to flow through. Around 15 g of particles were used, 14.660 g of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and 14.569 g of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$. An overview of the reactor setup can be seen in figure 3.3.

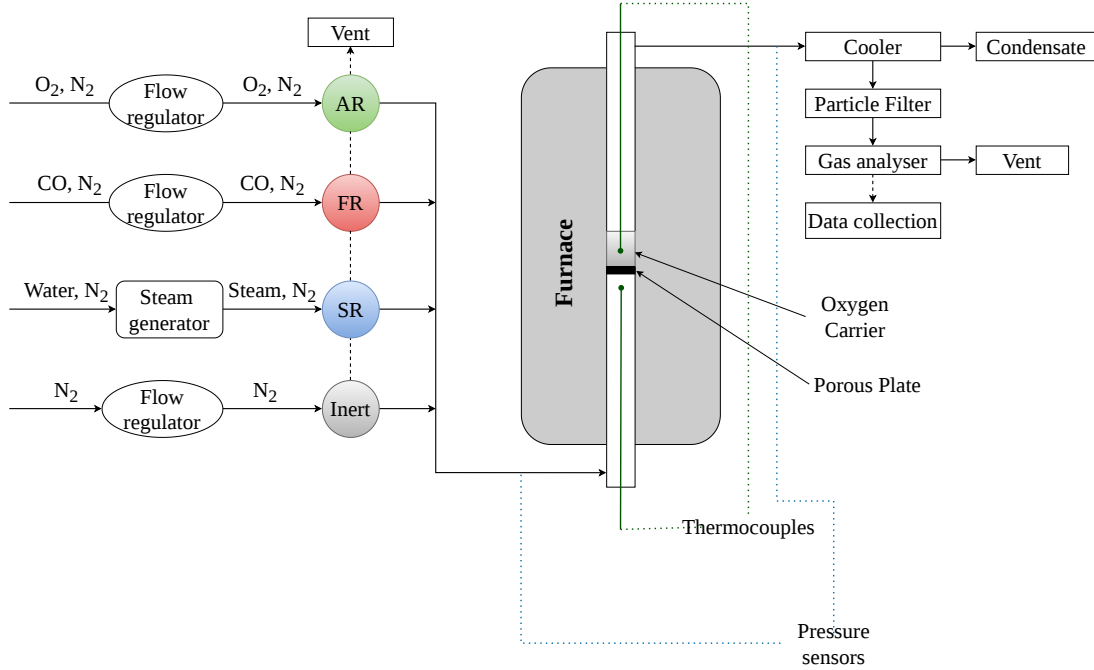


Figure 3.3: Overview of reactor setup for CLWS experiments.

The reactor was sealed and then mounted in an electrically heated furnace. The gas flows were regulated using flow regulators and the gases entering the reactor were controlled with magnetic control valves. The steam was generated using a steam generator wherein distilled water was evaporated and mixed with N₂. After exiting the reactor, the gases were cooled with a cooler and the condensate was separated to

ensure that no water entered the gas analyser. Heating cords were installed before and after the reactor to ensure that the steam did not condense before entering and after exiting the reactor. Two thermocouples were inserted into the reactor in order to monitor the reactor temperature with a measuring frequency of 1 Hz. The pressure drop over the reactor was monitored using two pressure sensors with a measuring frequency of 9 Hz. The gas analyser used was a Rosemount NGA 2000 which measured the volumetric flow rate and concentration of O_2 , CO_2 , H_2 and CO with a measuring frequency of 1 Hz.

3.3.2 Experiments

3.3.2.1 $Ca_{0.5}La_{0.5}FeO_{3-\delta}$

The experiments for the $Ca_{0.5}La_{0.5}FeO_{3-\delta}$ oxygen carrier were divided into two sections. The first section was with alternating AR and FR phases with intermittent inert phases. These were performed to "activate" the OC which was performed in order to get consistent gas conversion behaviour in the FR. The reduction time was gradually increased to observe the behaviour of the CO_2 gas concentration.

The second section, cycles 15, 16 and 17, was the same but with an added SR phase and inert phase to test the hydrogen production capacity and hydrogen production rate. They were all performed at 900 °C. The list of experiments performed with $Ca_{0.5}La_{0.5}FeO_{3-\delta}$ can be seen in table 3.5. Additional experiments with an SR phase were performed at different temperatures, however, the reactor defluidised at cycles 15 and 16 so the results of these experiments are not reliable. The table with the list of experiments performed after cycle 17 can be seen in appendix A.4.1.

Table 3.5: List of experiments performed with $Ca_{0.5}La_{0.5}FeO_{3-\delta}$ including the number of cycles and FR time. Cycles 15, 16 and 17 were also performed with an SR phase at 900°C.

Cycle	t_{FR} [s]	Cycle	t_{FR} [s]	Cycle	t_{FR} [s]
1	10 s	7	20 s	13	40 s
2	10 s	8	20 s	14	30 s
3	15 s	9	25 s	15	40 s
4	15 s	10	30 s	16	50 s
5	20 s	11	40 s	17	60 s
6	20 s	12	50 s		

3.3.2.2 $La_{0.5}Mg_{0.5}MnO_{3-\delta}$

The experiments for the $La_{0.5}Mg_{0.5}MnO_{3-\delta}$ oxygen carrier were performed in a similar way to the $Ca_{0.5}La_{0.5}FeO_{3-\delta}$ oxygen carrier. The first section with 15 cycles was with alternating AR and FR phases where the reduction time was gradually increased until the CO_2 concentration started decreasing at a reduction time of 110 s. The list of experiments in the first section with the cycle number and FR time can be seen in table 3.6.

Table 3.6: List of FR experiments performed with $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ including the number of cycles and FR time.

Cycle	t_{FR} [s]	Cycle	t_{FR} [s]	Cycle	t_{FR} [s]
1	5	6	30	11	70
2	10	7	35	12	80
3	15	8	40	13	90
4	20	9	50	14	100
5	25	10	60	15	110

The second section with the SR phase was performed at a consistent 120 s reduction time in order to compare the CO conversion in the FR of each cycle and keep the δ_{FR} value consistent between SR experiments. The temperature of the SR phase was also varied between 700°C and 900°C. Many cycles were deemed outliers due to the H_2 concentration behaving irregularly and repeats had to be performed. This is why there are different amounts of experiments for each temperature. The list of experiments in the second section with the cycle number and SR temperature can be seen in table 3.7. The outliers are in bold.

Table 3.7: List of SR experiments performed with $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ including the cycle number and SR temperature.

Cycle	T_{SR} [°C]	Cycle	T_{SR} [°C]	Cycle	T_{SR} [°C]
16	900	27	850	38	850
17	900	28	800	39	900
18	900	29	800	40	800
19	900	30	800	41	700
20	900	31	800	42	800
21	900	32	750	43	800
22	850	33	750	44	850
23	800	34	750	45	750
24	750	35	750	46	900
25	700	36	750		
26	850	37	700		

3.3.3 Performance Analysis of Oxygen Carrier Particles

In order to calculate $\Delta\delta$ for the fuel reactor and steam reactor equation 3.2 was used.

$$\Delta\delta = -\frac{\Delta m_{OC}}{m_{OC,0}} \frac{M_{OC}}{M_O} \quad (3.2)$$

$\Delta\delta$ is the difference in oxygen deficiency, Δm_{OC} is the difference in total mass of the oxygen carrier particles, $m_{OC,0}$ is the mass of the fully oxidised particles, M_{OC} is the molar mass of the oxygen carrier and M_O is the molar mass of oxygen. For the FR phase, the initial δ value was set to 0 and for the SR phase, the initial value

was set to the last value of the previous FR phase.

$\Delta m_{OC,FR}$ was calculated using the outflow of CO_2 from the reactor which was assumed to be an ideal gas. This is represented in equation 3.3.

$$\Delta m_{OC,FR} = -\frac{M_{O_2}P}{RT} \int_{t_1}^{t_2} \dot{V}_{CO_2} dt \quad (3.3)$$

P and T are the ambient pressure and temperature in the gas analyser and were assumed to be 1 atm and 25°C respectively, R is the ideal gas constant. t_1 and t_2 are the time boundaries of CO_2 in the flue gases and $\dot{V}_{CO_2}$ is the outflow of CO_2 . The integral was approximated using the trapezium rule.

The gas conversion of CO in the fuel reactor, γ_{CO} , was calculated using equation 3.4. By comparing the profile of γ_{CO} of the different cycles the performance of the particles can be evaluated as the particles undergo more cycles.

$$\gamma_{CO} = \frac{x_{CO_2}}{x_{CO} + x_{CO_2}} \quad (3.4)$$

x_{CO} and x_{CO_2} are the flue gas concentrations of CO and CO_2 respectively.

$\Delta m_{OC,SR}$ was calculated using the outflow of H_2 from the reactor which was also assumed to be an ideal gas. This is represented in equation 3.5.

$$\Delta m_{OC,SR} = \frac{M_{O_2}P}{RT} \int_{t_1}^{t_2} \dot{V}_{H_2} dt \quad (3.5)$$

$\dot{V}_{H_2}$ is the volumetric flow of H_2 out of the reactor.

In order to evaluate the kinetics of the OC:s as the δ value changed, the reaction rate with δ as its basis, $\frac{d\delta}{dt}$, was used. This describes the rate the reaction is occurring at, at different δ values. Due to delta decreasing in the SR phase, $-\frac{d\delta}{dt}$ was used instead. The derivatives were approximated using the central difference method.

The hydrogen production capacity, HPC, is the total amount of hydrogen that the OC can produce in units mmol g^{-1} . The hydrogen production capacity was calculated using equation 3.6.

$$HPC = \frac{P}{RTm_{OC}} \int_{t_1}^{t_2} \dot{V}_{H_2} dt \quad (3.6)$$

The hydrogen production capacity can also be calculated using $\Delta\delta_{SR}$ which can be seen in equation 3.7.

$$HPC = -\frac{\Delta\delta_{SR}}{M_{OC}} \quad (3.7)$$

In order to evaluate the kinetic performance of the OC:s, the Hydrogen Production

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rate (HPR) was used. HPR was calculated using equation 3.8 and it has the unit $\text{mmol g}^{-1} \text{min}^{-1}$.

$$HPR = \frac{HPC}{\Delta t} \quad (3.8)$$

Δt was the time it took for the H_2 gas concentration to reach 0.2%.

Due to the flow rate in the gas analyser struggling to accurately measure at flow rates below 600 mL min^{-1} the flow rate during the SR experiments had to be calculated from the H_2 gas concentration and the N_2 gas flow rate into the reactor. This is demonstrated in equation 3.9.

$$\dot{V}_{SR} = \frac{\dot{V}_{\text{N}_2}}{1 - x_{\text{H}_2}} \quad (3.9)$$

$\dot{V}_{SR}$ is the volume flow rate of the gases in the gas analyser, $\dot{V}_{\text{N}_2}$ is the gas flow rate of N_2 into the reactor and x_{H_2} is the H_2 gas concentration.

In order to determine if the reactor defluidised at any point, the gradient of the pressure drop in the reactor, $\frac{d\Delta P}{dt}$, was plotted against time. When a fluidised bed reactor defluidises, the pressure drop fluctuations decrease and so does $\frac{d\Delta P}{dt}$. $\frac{d\Delta P}{dt}$ was approximated using the central difference method.

4

Results

4.1 Calcination Results

In this section the results from the calcination are presented, as well as the yield and bulk densities of the different particles.

In figure 4.1 the perovskite oxygen carrier particles after calcination can be seen. $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ was black and the particles were hard and difficult to crush compared to the others. $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ was grey and was softer than $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ but still harder than $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$. $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ were very similar in colour and hardness and were much softer than $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$. Figures of the other batches of perovskite oxygen carriers can be seen in appendix A.1.



Figure 4.1: 5g samples of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ after calcination. From left to right: $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$.

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In table 4.1 the mass yields of the large batches of perovskite oxygen carrier particles are shown. Most of the yields were between 38 % and 44 % with one outlier being the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles calcined at 1250 °C.

Table 4.1: Mass yield of the large batches of perovskite metal oxides.

Oxygen carrier	Yield [%]
$\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ (30 g, 1250°C)	38.0 %
$\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ (40 g, 1250°C)	53.3 %
$\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ (40 g, 1250°C)	41.5 %
$\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ (40 g, 1250°C)	40.3 %
$\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ (40 g, 1300°C)	41.3 %
$\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ (40 g, 1300°C)	43.8 %

In table 4.2 the bulk densities of different 40 g samples of perovskite metal oxide oxygen carriers is shown. Note that this was not performed for $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ because it fluidised without issue. Note also that it could not be performed for the 40 g batches of $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ calcined at 1250 °C because most of the sample had been used in the reactor and there was an insufficient amount of both used and unused particles.

Table 4.2: Bulk densities of three different perovskite oxygen carrier particles, calcined at different temperatures.

Oxygen carrier	Bulk density [g cm^{-3}]
$\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ (1250 °C)	0.978
$\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ (1300 °C)	1.03
$\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ (1300 °C)	1.30

4.2 XRD results

In figure 4.2 the diffractograms of the perovskite metal oxides can be seen. The stars represent an identified perovskite phase and the name of the identified phase can be seen as well. $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ were identified to have pure perovskite structure whereas $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ had some spinel structure impurities with the chemical structure AB_2O_4 . The Y-bearing perovskites have a different crystal structure to the non Y-bearing perovskites. The Y-bearing perovskites are orthorhombic, whereas $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ are cubic. The diffractograms, including the ones for the large batches can be seen in appendix A.2.

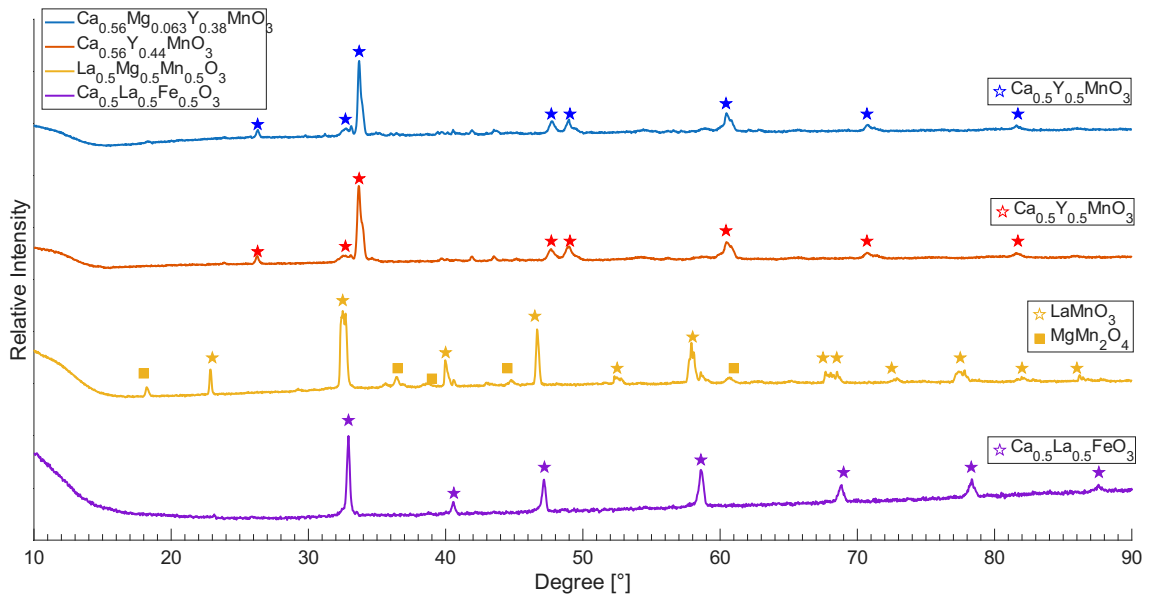


Figure 4.2: Diffractograms of 5 g samples of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$.

4.3 CLWS results

In this section the CLWS results for the oxygen carriers $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ calcined at 1250 °C and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ calcined at 1300 °C are presented.

4.3.1 $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$

In this section the CLWS results for $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ are presented, then the results from the steam reactor, finally the results involving defluidisation of the reactor will be presented.

4.3.1.1 Fuel reactor results

In figure 4.3 the fuel conversion, γ_{CO} , in the fuel reactor, is plotted against the oxygen deficiency, δ_{FR} , in the FR for 17 total cycles. The conversion starts at 1 for every cycle and then at around a δ_{FR} value of 0.02 it starts to decrease until it starts to plateau at a δ_{FR} value of 0.065. γ_{CO} settles at a value of 0.2. Two cycles is an outliers, that being cycles 14 and 15, where γ_{CO} starts decreasing from 1 immediately until plateauing at the same γ_{CO} value as the other cycles. Cycles 16 and 17 are also slightly different. The δ_{FR} value where the γ_{CO} value starts decreasing is the same but γ_{CO} decreases slightly more and the curves are parallel to the others. The largest δ_{FR} value was 0.085, achieved in cycle 17.

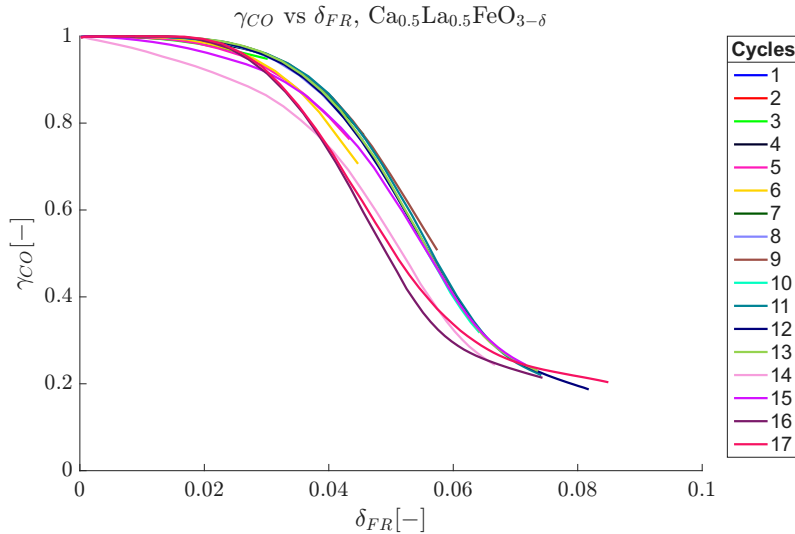


Figure 4.3: Fuel conversion, γ_{CO} , plotted against oxygen deficiency, δ_{FR} , in the fuel reactor for $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$.

In figure 4.4 the reaction rate in the FR, $\frac{d\delta_{FR}}{dt}$, is plotted against oxygen deficiency, δ_{FR} for 17 total cycles. $\frac{d\delta_{FR}}{dt}$ for all cycles starts by increasing rapidly until δ_{FR} reaches 0.025 and then decreasing slowly until δ is between 0.06 and 0.07 where $\frac{d\delta_{FR}}{dt}$ starts to plateau. This mirrors the behaviour of γ_{CO} where conversion is 1 until δ_{FR} reaches 0.025 where it then decreases until δ_{FR} reaches between 0.06 and 0.07 where it then plateaus.

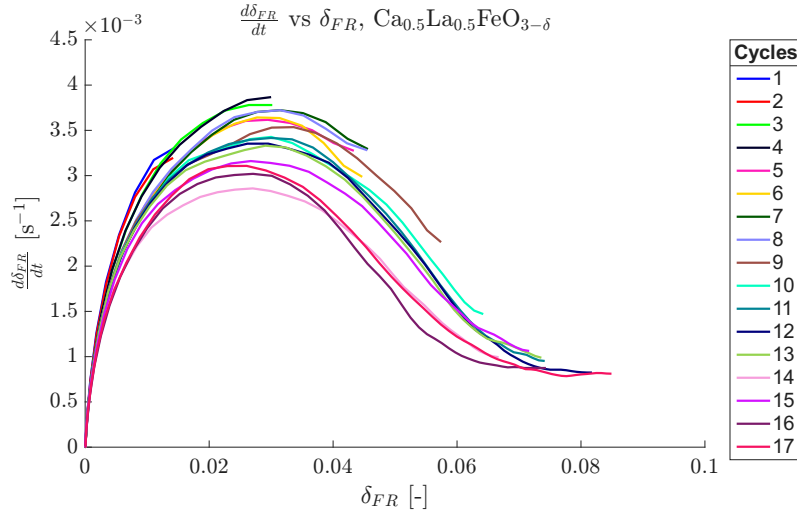


Figure 4.4: Rate of change of oxygen deficiency, $\frac{d\delta}{dt}$, plotted against oxygen deficiency, δ_{FR} .

4.3.1.2 Steam reactor results

In figure 4.5 the reaction rate in the SR, $-\frac{d\delta_{SR}}{dt}$, is plotted against δ_{SR} . Cycle 15 has the largest peak followed by cycle 16. Cycle 17 has the smallest peak of the three SR cycles. The $\Delta\delta_{SR}$ values are all slightly different with cycle 15 being the largest and cycle 16 being the smallest.

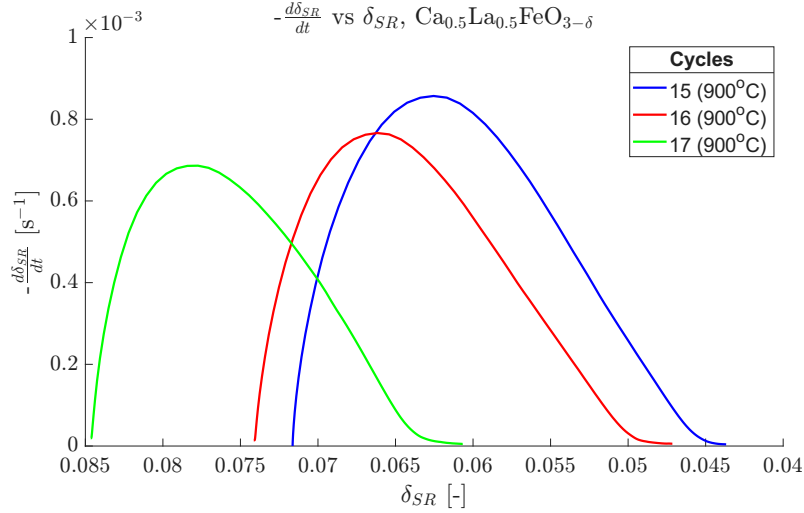


Figure 4.5: $-\frac{d\delta_{SR}}{dt}$ plotted against δ_{SR} , $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$.

In the beginning of the SR phase in the fifteenth and sixteenth cycles the pressure drop fluctuations decreased significantly. This can be seen in figure 4.6 where the gradient of the pressure drop in the reactor, $\frac{d\Delta P}{dt}$, is shown. At around 4500 s the $\frac{d\Delta P}{dt}$ decrease lasted around 10-15 s and at around 5800 s the $\frac{d\Delta P}{dt}$ decrease lasted around 100-110 s. After a short period of time the reactor refluidised in both Cycles during the SR phase. This however did not cause the agglomerates to completely break apart. When the particles were removed from the reactor, many agglomerates

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were observed. The list of experiments performed after defluidisation along with γ_{CO} , $\frac{\delta_{FR}}{dt}$ and $-\frac{\delta_{SR}}{dt}$ plots can be seen in appendix A.4.1.

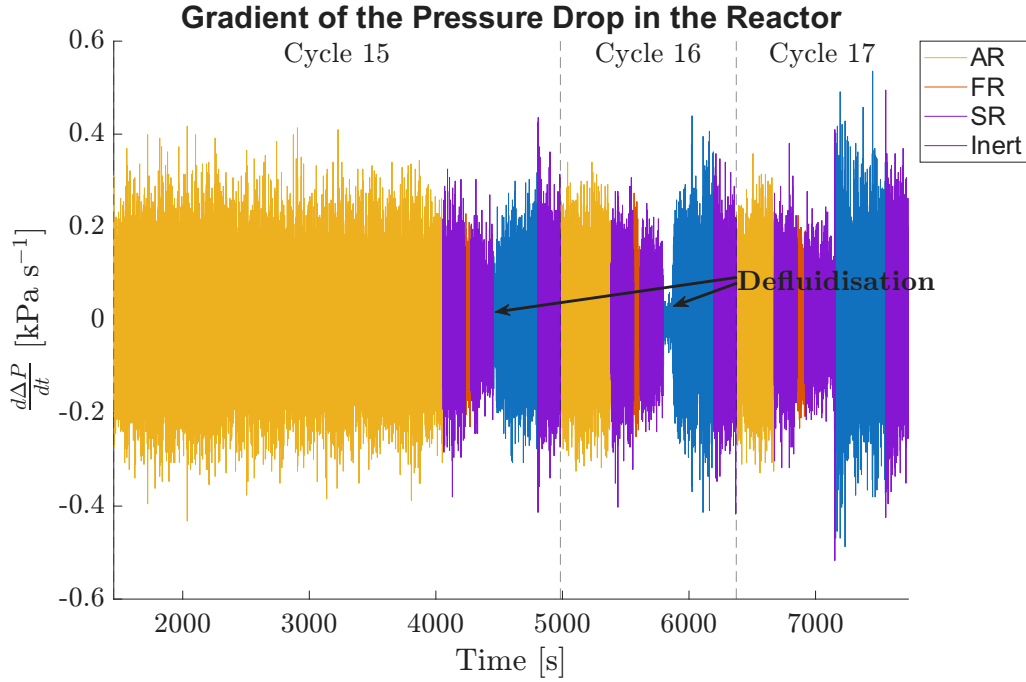


Figure 4.6: $\frac{d\Delta P}{dt}$ for cycles 14-17, including startup and shutdown of reactor with defluidisation occurring during the SR phase of cycle 15 and 16.

The effects of defluidisation can be seen in table 4.3 where the hydrogen production capacity and hydrogen production rate are presented for cycle 15, 16 and 17 for CLWS experiments with $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$. The HPR of cycles 16 and 17 are 20-30% smaller than the HPR of cycle 15. The HPC of cycles 15 and 16 are similar with the HPC of cycle 17 being 10-15% smaller than cycles 15 and 16.

Table 4.3: HPC and HPR for SR cycles at 900°C, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$.

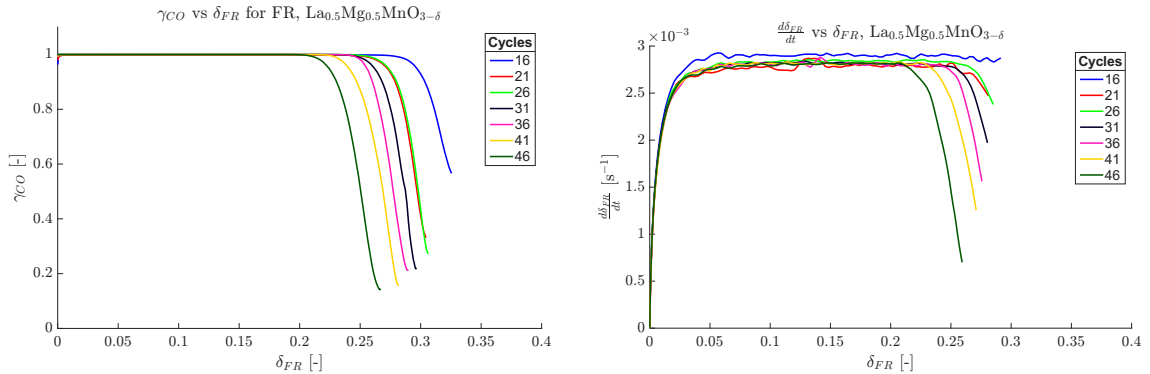
Cycle	HPC [mmol g ⁻¹]	HPR [mmol g ⁻¹ min ⁻¹]
15	0.1458	0.0511
16	0.1418	0.0399
17	0.1265	0.0350

4.3.2 $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$

In this section the CLWS results for $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ calcined at 1300 °C are presented, including the FR results and the SR results for the different temperatures.

4.3.2.1 Fuel reactor results

In figure 4.7 the CO conversion, γ_{CO} , and the reaction rate, $\frac{d\delta_{FR}}{dt}$, are plotted against the oxygen deficiency, δ_{CO} , in the fuel reactor. This is done for every fifth FR phase starting with cycle 16 and finishing with cycle 46. All 7 cycles have the same reduction time of 120s. For cycles 1-15 no decrease, or a very small decrease, in γ_{CO} can be seen and they are therefore not shown in figure 4.7. In figure 4.7a γ_{CO} is plotted and there is a clear trend where γ_{CO} starts decreasing at smaller δ_{SR} values the more cycles that have been performed. The same trend can be seen in figure 4.7b where $\frac{d\delta_{FR}}{dt}$ starts also decreasing at smaller δ_{SR} values the more cycles that have been performed. The largest δ_{FR} value was 0.326, achieved in cycle 16. The rest of the FR plots for $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ can be seen in appendix A.4.2. Note that for figure 4.7a the γ_{CO} and δ_{SR} values are plotted for an extended period of 20 s after the phase has changed to inert whereas for figure 4.7b γ_{CO} and δ_{FR} are only plotted during the FR phase. This was because the presence of inert gas in the flue gases gives false information about reaction rate but not CO conversion.



(a) γ_{CO} plotted against δ_{FR} for cycles 16, 21, 26, 31, 36, 41 and 46, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

(b) $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 16, 21, 26, 31, 36, 41 and 46, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

Figure 4.7: γ_{CO} and $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} , $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

4.3.2.2 Steam reactor results

In this section the steam reactor results are presented for $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, starting with the mean HPC and mean HPR values for the SR experiments performed at different temperatures. After that, the reaction rate, $\frac{d\delta_{SR}}{dt}$, plotted against δ_{SR} is presented for the different cycles at different temperatures.

In table 4.4 the mean hydrogen production capacity ($\overline{HPC}$) and mean hydrogen production rate ($\overline{HPR}$) are shown for SR experiments performed at 700 °C, 750 °C, 800 °C, 850 °C and 900 °C. There is no clear trend for the $\overline{HPC}$ or the $\overline{HPR}$.

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Experiments performed at 800 °C and above had higher $\overline{HPC}$ values than the experiments at lower temperatures. Experiments performed at 800 °C and below had smaller $\overline{HPR}$ values. Experiments performed at 800 °C had the largest $\overline{HPC}$ value and experiments performed at 850 °C had the largest $\overline{HPR}$ value.

Table 4.4: Mean HPC ($\overline{HPC}$) and mean HPR ($\overline{HPR}$) for SR cycles at 700 °C - 900°C, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

Temperature [°C]	$\overline{HPC}$ [mmol g ⁻¹]	$\overline{HPR}$ [mmol g ⁻¹ min ⁻¹]
900 °C	0.176	0.040
850 °C	0.162	0.042
800 °C	0.179	0.035
750 °C	0.135	0.031
700 °C	0.154	0.035

In figure 4.8 the reaction rate in the steam reactor, $-\frac{d\delta_{SR}}{dt}$, is plotted against δ_{SR} for Sr experiments performed at 900°C. Cycles 16,18,21 and 46 have similar shapes, peak $-\frac{d\delta_{SR}}{dt}$ values and a similar $\Delta\delta_{SR}$. Cycle 17 and 39 have larger peaks and larger $\Delta\delta_{SR}$. All cycles start and end at different δ_{SR} values.

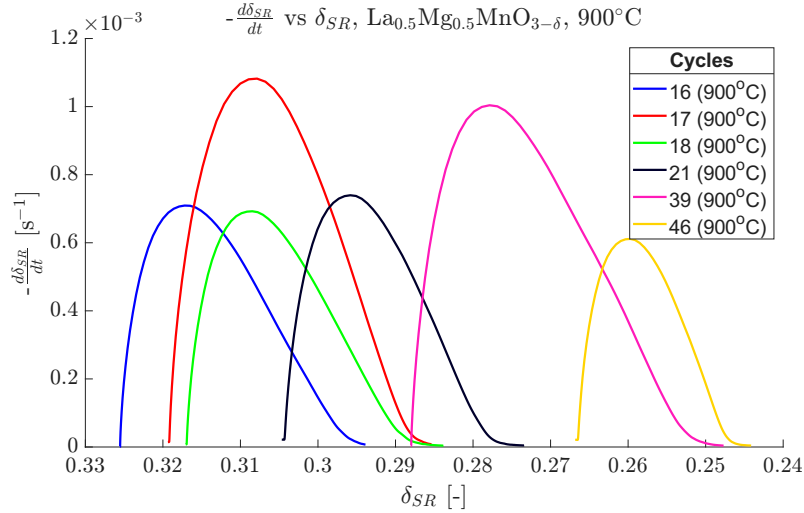


Figure 4.8: $-\frac{d\delta_{SR}}{dt}$ plotted against δ_{SR} at 900 °C, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

In figure 4.9 the reaction rate in the steam reactor, $-\frac{d\delta_{SR}}{dt}$, is plotted against δ_{SR} for SR experiments performed at 850°C. Cycles 26, 27, 38 and 44 have similar shapes and peak $-\frac{d\delta_{SR}}{dt}$ values with cycle 27 having the smallest peak $-\frac{d\delta_{SR}}{dt}$ value and cycle 38 having the largest peak $-\frac{d\delta_{SR}}{dt}$ value of these. Cycle 22 has a different shape where the $-\frac{d\delta_{SR}}{dt}$ value doesn't decrease smoothly like the others. Cycles 22, 26 and 27 start and finish at similar δ_{SR} values. Cycles 38 and 44 start and finish at very different values to the others. All cycles have similar $\Delta\delta_{SR}$ values with cycle 38 having the largest $\Delta\delta_{SR}$ value.

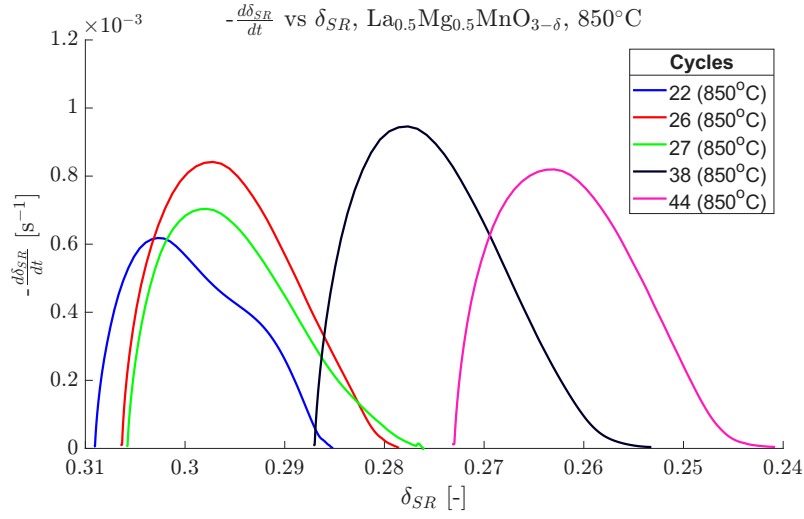


Figure 4.9: $-\frac{d\delta_{SR}}{dt}$ plotted against δ_{SR} at 850 °C, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

In figure 4.10 the reaction rate in the steam reactor, $-\frac{d\delta_{SR}}{dt}$, is plotted against δ_{SR} for SR experiments performed at 800 °C. cycles 28, 29, 30, 31 and 43 all have similar shapes, peak $-\frac{d\delta_{SR}}{dt}$ values and $\Delta\delta_{SR}$ values. Cycles 28, 29 and 31 start and finish at similar δ_{SR} values. Cycle 43 and 40 start and finish at very different δ_{SR} values to the others. Cycle 40 also has a larger peak $-\frac{d\delta_{SR}}{dt}$ value than the others.

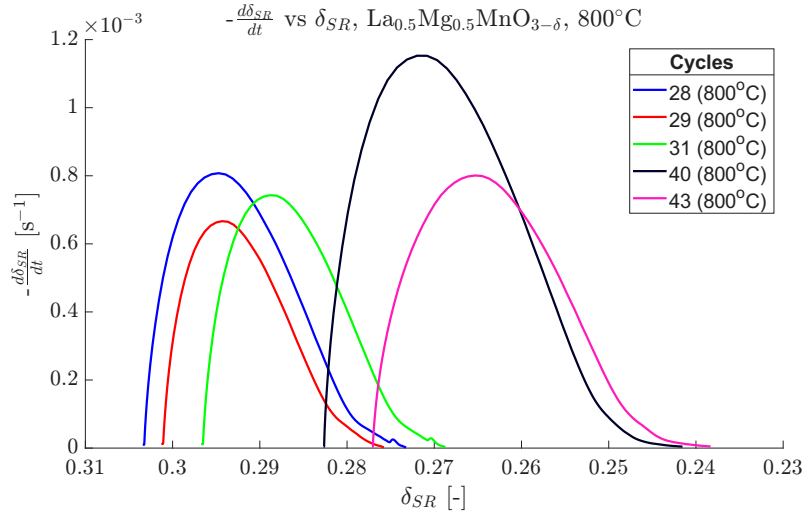


Figure 4.10: $-\frac{d\delta_{SR}}{dt}$ plotted against δ_{SR} at 800 °C, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

In figure 4.11 the reaction rate in the steam reactor, $-\frac{d\delta_{SR}}{dt}$, is plotted against δ_{SR} for SR experiments performed at 750 °C. All cycles had very different peak $-\frac{d\delta_{SR}}{dt}$ values and $\Delta\delta_{SR}$ values. Cycle 36 had by far the largest of both of these. All cycles also started and finished at different δ_{SR} values.

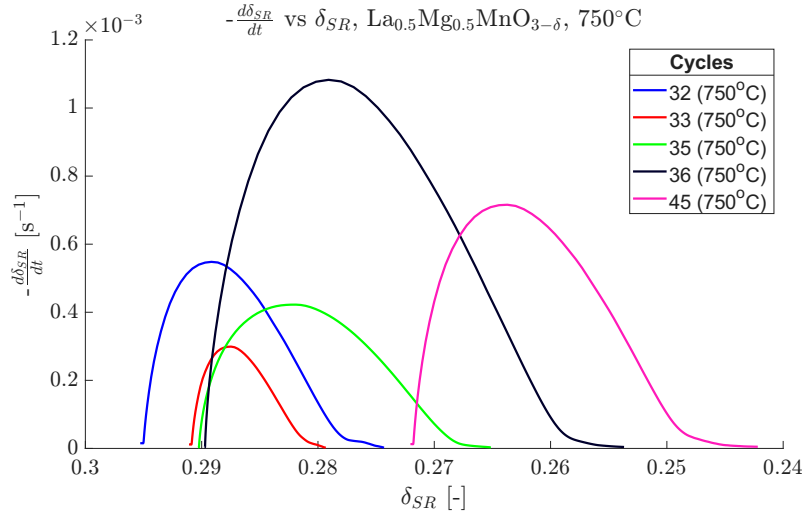


Figure 4.11: $-\frac{d\delta_{SR}}{dt}$ plotted against δ_{SR} at 750°C , $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

In figure 4.12 the reaction rate in the steam reactor, $-\frac{d\delta_{SR}}{dt}$, is plotted against δ_{SR} for SR experiments performed at 700°C . cycles 41 and 37 have similar $\Delta\delta_{SR}$ values with cycle 37 having the larger peak $-\frac{d\delta_{SR}}{dt}$ value and $\Delta\delta_{SR}$ value. They also start and finish at similar δ_{SR} values. Cycle 25 has a much smaller peak $-\frac{d\delta_{SR}}{dt}$ value and $\Delta\delta_{SR}$ value. It also starts and finishes at very different δ_{SR} values.

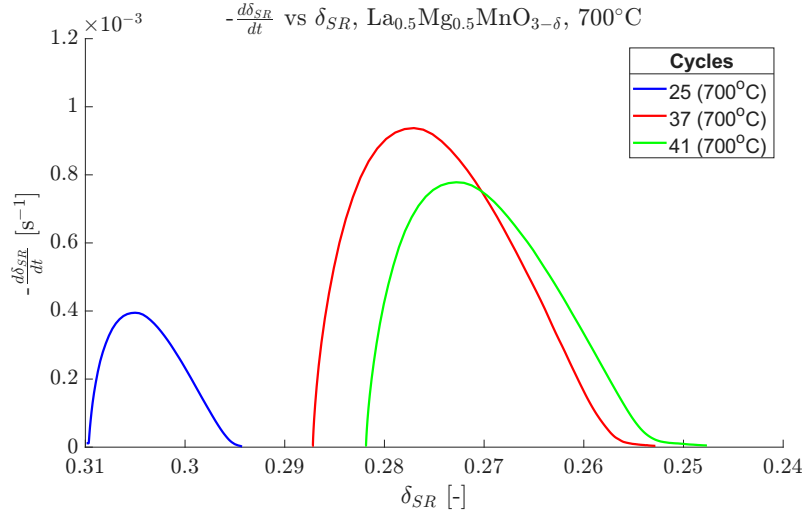


Figure 4.12: $-\frac{d\delta_{SR}}{dt}$ plotted against δ_{SR} at 700°C , $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

4.3.3 Summary of SR results

In table 4.5 a comparison of the HPR values of different oxyfen carriers can be seen. The values chosen are the largest attained for the different OC:s and the temperature chosen for $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ and magnetite fines was the temperature that gave the largest HPR. The HPR for the magnetite fines was taken from a previous study by Staničić et al [7]. Magnetite fines is an enriched iron ore product with a 98 wt % iron oxide content. The magnetite fines have a significantly higher HPR value than the two perovskite metal oxides used for CLWS in this study.

Table 4.5: Comparison of HPR and HPP of different oxygen carriers.

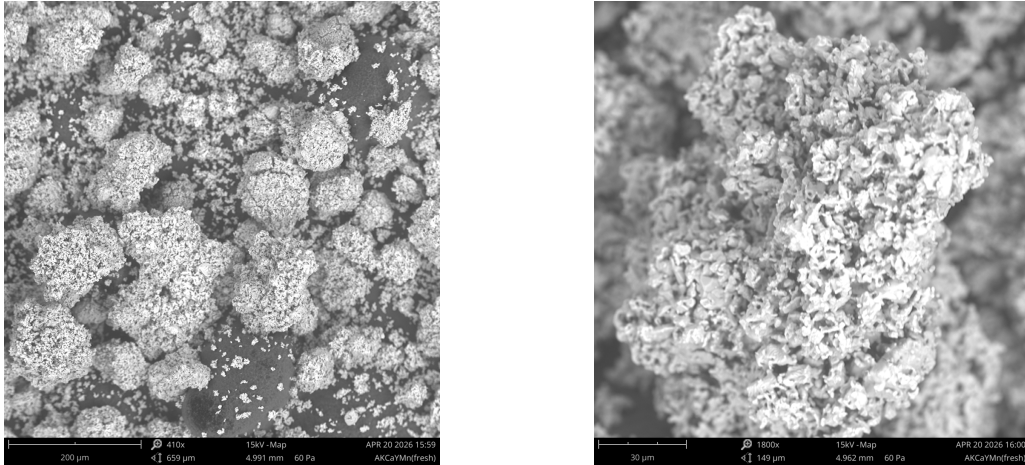
Oxygen Carrier	HPC [mmol g ⁻¹]	HPR [mmol g ⁻¹ min ⁻¹]
Ca _{0.5} La _{0.5} FeO _{3-δ} (900 °C)	0.1458	0.051
La _{0.5} Mg _{0.5} MnO _{3-δ} (850 °C)	0.162	0.042
Magnetite Fines (800 °C)	1.75	0.37

4.4 SEM-EDS results

In this section the SEM micrographs for all oxygen carrier particles are presented, including the particles not used in batch fluidised bed experiments, Ca_{0.56}Mg_{0.063}Y_{0.38}MnO_{3-δ} and Ca_{0.56}Y_{0.44}MnO_{3-δ}.

4.4.1 Ca_{0.56}Y_{0.44}MnO_{3-δ} and Ca_{0.56}Mg_{0.063}Y_{0.38}MnO_{3-δ}

In figure 4.13 two micrographs of Ca_{0.56}Y_{0.44}MnO_{3-δ} are shown. In the micrograph to the left, figure 4.13a an overview of several different particles can be seen. They are all porous. There is also a lot of dust in the background. In micrograph to the right, figure 4.13b, there is a micrograph of one particle with a larger magnification. This particle is porous and doesn't have a smooth general shape due to the sharp edges and porosity.



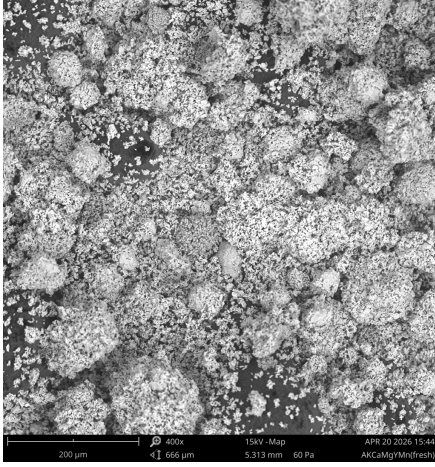
(a) Micrograph of Ca_{0.56}Y_{0.44}MnO_{3-δ} particles, 410× magnification.

(b) Micrograph of a Ca_{0.56}Y_{0.44}MnO_{3-δ} particle, 1800× magnification.

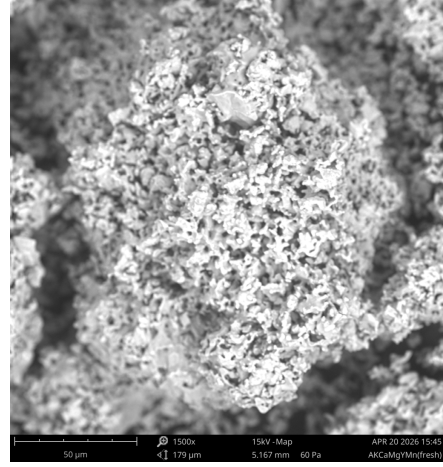
Figure 4.13: Micrograph of Ca_{0.56}Y_{0.44}MnO_{3-δ} particles with different magnifications, one smaller and one larger.

In figure 4.14 two micrographs of Ca_{0.56}Mg_{0.063}Y_{0.38}MnO_{3-δ} are shown. In figure 4.14a an overview of several Ca_{0.56}Mg_{0.063}Y_{0.38}MnO_{3-δ} particles can be seen. They have a similar appearance to the Ca_{0.56}Y_{0.44}MnO_{3-δ} particles but slightly smoother and equally porous. In figure 4.14b a micrograph with a larger magnification of a

single particle. It is similar in appearance to the $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ particle, porous with rough edges.



(a) Micrograph of $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ particles, 400 $\times$ magnification.



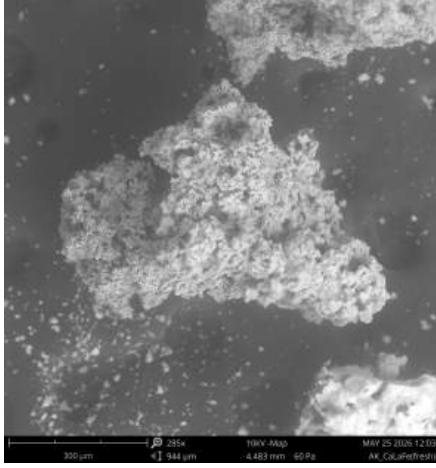
(b) Micrograph of a $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ particle, 1500 $\times$ magnification.

Figure 4.14: Micrograph of $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ particles with different magnifications, one smaller and one larger.

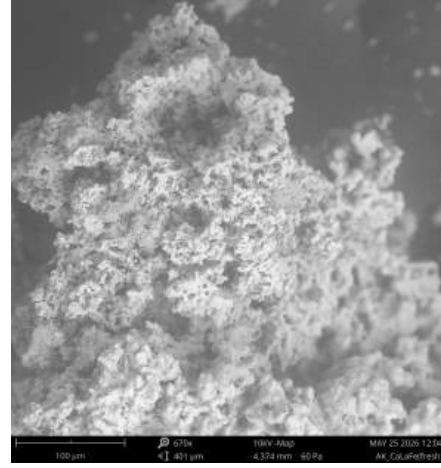
4.4.2 $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$

4.4.2.1 $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$

In figure 4.15 two micrographs of a $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle can be seen. In figure 4.15a the whole particle can be seen. The particle is porous with sharp edges. In the micrograph with a larger magnification, figure 4.15b the particle can be seen with finer detail.



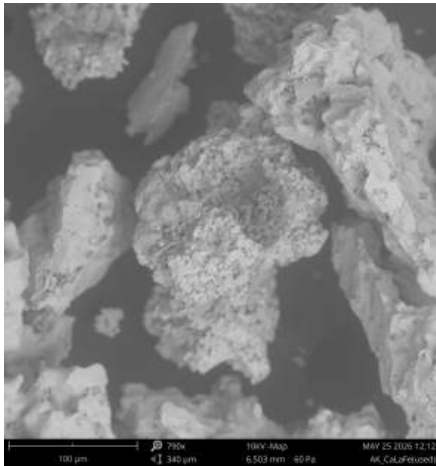
(a) Micrograph of an unused $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle, 285 $\times$ magnification.



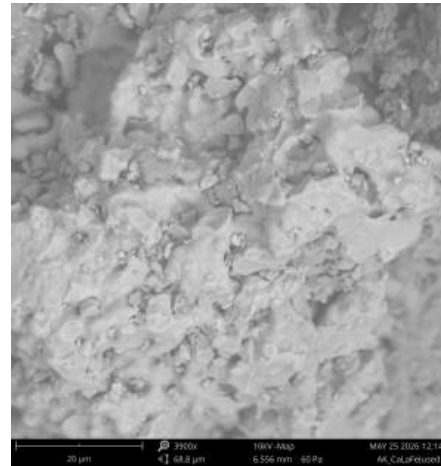
(b) Micrograph of an unused $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle, 670 $\times$ magnification.

Figure 4.15: Micrograph of an unused $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle with different magnifications, one smaller and one larger.

In figure 4.16 two micrographs of a $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle can be seen. In figure 4.16a the whole particle can be seen as well as a few nearby ones. In comparison to the unused $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle in figure 4.15a the particle looks less porous and more smooth. Comparing the micrographs with larger magnifications in figures 4.15b and 4.16b the used $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle can also be seen to be more smooth.



(a) Micrograph of a used $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle, 790 $\times$ magnification.

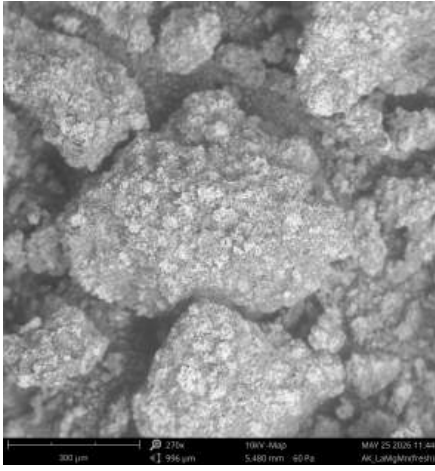


(b) Micrograph of a used $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle, 3900 $\times$ magnification.

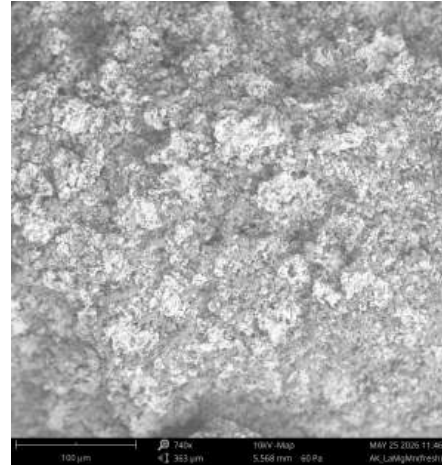
Figure 4.16: Micrograph of a $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particle after 25 cycles with different magnifications, one smaller and one larger.

4.4.2.2 $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$

In figure 4.17 micrographs of an unused $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle can be seen. Compared to the previously mentioned particles, the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles were less porous. There was also two different shades of grey on the particle, one light and one dark. Using EDS to analyse the composition of these respective parts, the light part consisted mainly of La with some Mn and very little Mg. The dark part consisted of Mn and Mg with very little La. The light phase was similar in appearance to the other particles whereas the dark phase had a different texture. It was not very porous and it had the appearance of small connected spheres. The EDS analysis tables with corresponding SEM micrographs can be seen in appendix A.3.



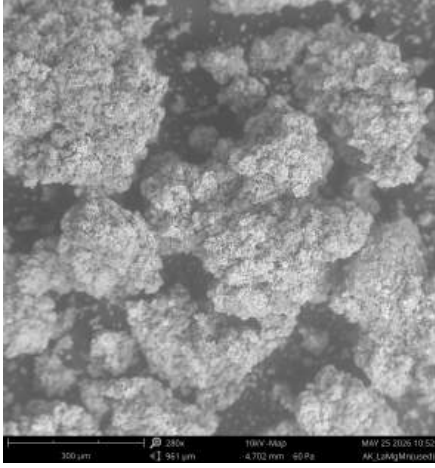
(a) Micrograph of an unused $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle, 270 $\times$ magnification.



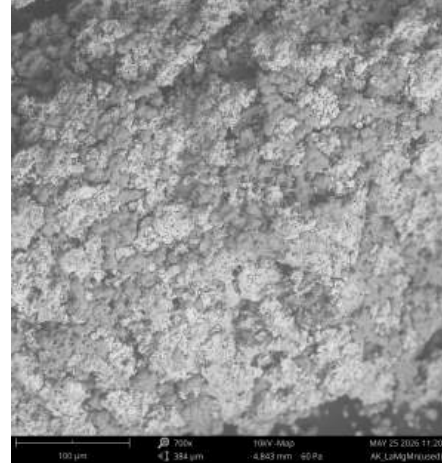
(b) Micrograph of an unused $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle, 740 $\times$ magnification.

Figure 4.17: Micrographs of an unused $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle with different magnifications, one smaller and one larger.

In figure 4.18 two micrographs of used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles can be seen. In figure 4.18a a micrograph of a few particles can be seen. Compared to the unused $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle, the used ones have a more rough shape and aren't as jagged. In figure 4.18b a micrograph with a larger magnification of a $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle can be seen. Compared to the unused $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle in figure 4.17b the used one is more porous. The same light and dark regions can also be observed. The EDS results for the light and dark regions gave very similar result to the unused particle, see appendix A.3.



(a) Micrograph of used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles, 280 $\times$ magnification.



(b) Micrograph of a used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle, 700 $\times$ magnification.

Figure 4.18: Micrographs of a $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particle after 46 cycles with different magnifications, one smaller and one larger.

5

Discussion

The performance of the studied perovskite metal oxides as oxygen carriers for CLWS had significantly smaller HPC and HPR values than the magnetite fines in the study by Staničić et al. The HPC of the magnetite fines was 12 times larger than $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and 9.8 times larger than $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$. The HPR of the magnetite fines was 7.25 times larger than $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and 8.8 larger than $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$. The reason for this is that for both $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ the conversion of the SR is highly limited by the equilibrium δ_{SR} , with the $\Delta\delta_{SR}$ values for both oxygen carriers being around 0.03-0.04. As can be seen in the figures where the reaction rate, $-\frac{d\delta_{SR}}{dt}$, decreases significantly for both oxygen carriers as the δ_{SR} value approaches equilibrium. In order to increase performance of the perovskite OC:s, the particles would need to be reduced further.

For the $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particles this would not be possible. This is because when the particles were reduced beyond a certain point, the particles sintered together and agglomerated causing the reactor to become partially defluidised. This has two consequences. First of all, the particles would no longer be able to be used in a CLWS system due to them not being able to be moved between the reactors easily. Second of all, the kinetics of the SR were significantly impacted. This can be seen in table 4.3 where the HPR values of the two cycles where after significant defluidisation occurred are significantly smaller despite similar HPC values. The kinetics of the FR were also impacted where for the FR phase after defluidisation (cycles 16-17) the conversion starts decreasing at an earlier points due to slower kinetics.

The reason that the reactor defluidised in the SR phase and not the FR phase could be because the FR phase is endothermic whereas the SR phase is exothermic. The heat produced by reaction 2.7 could have caused the particles to sinter together and agglomerate when the particles were reduced beyond a certain point. Other possible causes of defluidisation are static electricity and dust buildup due to of particle attrition. Cycles 11-13 had reduction times of 40-50s. Despite this, the reactor did not defluidise. This is likely because as the particles underwent more and more cycles, more attrition of the particles occurred which decreased the mass of particles in the reactor. This causes the particles remaining in the reactor to be reduced further, increasing δ_{FR} .

It is possible to reduce the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles further due to no defluidisation occurring. However as seen in figure 4.7a the CO conversion decreases rapidly towards the end of the FR phase. This means that the δ_{FR} value is approaching

equilibrium and the particles cannot be reduced much further. The $\Delta\delta_{SR}$ values are quite small, however, which means that an increase of δ_{FR} by 0.03 would almost double the HPC. This would also have a large effect on the HPR values. Considering how much smaller the HPR value of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ is compared to the magnetite fines its unlikely that the increase would be meaningful enough to improve performance above that of the magnetite fines.

Due to the HPC values of both $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, it is possible that a different perovskite metal oxide oxygen carrier could outperform the magnetite fines. This is because the kinetics of the FR are very good, at least for $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$. The CO conversion remains 100 % until the δ_{FR} is quite close to equilibrium. The equilibrium points for the FR and SR would need to be further apart which could cause the conversion decrease further away from the equilibrium point, but more research needs to be done on more different perovskite metal oxides to determine this.

One interesting phenomenon for the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles is that the $\Delta\delta_{SR}$ values are similar for the different temperatures. Thermodynamically the equilibrium δ_{SR} value should decrease with lower temperatures causing the $\Delta\delta_{SR}$ to increase and thus increasing the HPC. One possible explanation for this is that there is some sort of phase transition occurring in the particles where the metal ions change oxidation state to accommodate oxygen atoms leaving the crystal lattice. When oxygen atoms are then added back in through reaction 2.7 the oxidation states change again, but only some oxidation state changes can be facilitated by steam oxidation which causes a hard limit to how far steam can oxidise the reduced $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles. A similar phenomenon is observed with the HPR values for temperatures between 800°C and 900°C being very similar. This could be because the reactions all happen very close to the same equilibrium causing similar reaction rates to be observed.

For both $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ the values of δ_{FR} for which the production of hydrogen starts and stops differs a significant amount between different cycles, despite identical experimental conditions. This is due to the flow rate fluctuations in the reactor having a higher frequency than the gas analyser is able to measure. This causes the calculated $\Delta\delta_{FR}$ values to be slightly different even when they should be the same. The difference in $\Delta\delta_{FR}$ values caused by this is around 0.03 which is similar in size to the $\Delta\delta_{SR}$ values. If the $\Delta\delta_{SR}$ values were larger, then this error, caused by the low measuring frequency relative to the flow rate fluctuations, would not be significant. There is also a small variance between the different FR cycles. This variance causes some of the SR phases to have very different peak $-\frac{d\delta_{SR}}{dt}$ values with some being very large and some being very small, despite the reduction phase having the same length. The high peaks also coincide with larger $\Delta\delta_{SR}$ values, which is reasonable, due to the reaction rate being highly dependant on distance from equilibrium. This needs to be taken into consideration for the $\overline{HPC}$ values where the variance isn't necessarily caused by randomness in the SR and worse particle performance, but also the variance of the FR which doesn't

impact the HPC value in the same way.

The impact of the $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particles undergoing 26 cycles and the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ undergoing 46 cycles on the particles morphology is different. The $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particles look a lot less porous and the surfaces are more smooth. This was caused by the sintering of the particles during defluidisation where the particles fused together. When these were then knocked loose from each other, smooth surfaces were left behind. No smooth surfaces can be seen on the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles and these particles did not defluidise. The used particles in figure 4.18 are more porous than the unused particles in figure 4.17. This was caused by attrition of the particles during the batch fluidised bed experiments where small parts of the particles were knocked loose after colliding.

The reason that the $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ particles didn't fluidise could be due to the low density of the particles. The low density could have caused the gases entering the reactor to form channels, bypassing the particles instead of fluidising them. The same could then be true for why the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles didn't fluidise when calcined at 1250 °C but did when calcined at 1300 °C. The density when calcined at 1250 °C was too low.

The $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles had two phases in the powder XRD diffractogram, one perovskite phase and one spinel phase. In the EDS analysis two phases were also identified, one light containing large amounts of La and one dark phase containing small amounts of La. This was the case for both used and unused $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles. The light phase is likely the perovskite phase seen in the XRD diffractogram in figure 4.2 with it consisting mainly of $\text{LaMnO}_{3-\delta}$ with small amounts of Mg on the A site. The dark phase is then the spinel phase seen in figure 4.2 with it containing mostly Mn and Mg with some La.

Comparing the predicted crystal structure of the OC:s in table 3.1 with the crystal structures measured with XRD, seen in figure 4.2, the measured crystal structure of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ matched the predicted cubic crystal structure, whereas for $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$, the measured crystal structure was orthorhombic instead of cubic. The reason that the crystal structure of $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ was orthorhombic and not cubic, is that the Goldschmidt tolerance factor was less than one, which means that the structure is not ideal, causing distortion of the crystal lattice. Despite the Goldschmidt tolerance factors of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ being smaller than that of $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$, the crystal structure did not distort away from the ideal cubic structure. The chemical composition of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ are very different from $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$ which causes the value of f where the crystal structure distorts to be different.

6

Conclusions

Four different perovskite metal oxides were successfully synthesised, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$, with $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ having spinel structure impurities. The first two, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ were able to be successfully fluidised and used in a batch reactor to simulate a continuous CLWS system. Both $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ underperformed compared to the iron oxide oxygen carrier, magnetite fines, with significantly smaller HPC and HPR values. The $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particles also sintered and agglomerated causing the HPC to be very limited. This happened after repeated FR phases when δ_{FR} went above 0.07. The HPC of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ wasn't limited by defluidisation but instead by thermodynamics and although the maximum possible amount of hydrogen wasn't produced it is unlikely that reaching equilibrium in the FR would lead to a significant enough increase of the HPR value to increase it above the HPR value of the magnetite fines. The HPC values for $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ were also not strongly dependent on temperature meaning that there could be some form of phase transition limiting the reaction instead of thermodynamics. The HPC value of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ was $0.1458 \text{ mmol g}^{-1}$ at 900°C and the HPR value was $0.051 \text{ mmol g}^{-1} \text{ min}^{-1}$ at 900°C . The largest HPC value of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ was $0.179 \text{ mmol g}^{-1}$ at 800°C and the largest HPR value was $0.042 \text{ mmol g}^{-1} \text{ min}^{-1}$ at 850°C .

The $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ and $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles both experienced worse γ_{CO} in the FR as more cycles were performed, with the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles undergoing 20 more cycles and a having larger performance decrease. The $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles did not defluidise. After undergoing 46 cycles, the $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ particles became more porous and fragmented with very little change to the surface. They were largely intact after undergoing 46 cycles. The $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particles morphology changed more drastically due to the sintering of some of the particles. Smooth surfaces were observed on the used $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particles that weren't observed on the unused $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ particles.

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A

Appendix

A.1 Calcination results



Figure A.1: 30-40 g samples of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_3$, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_3$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_3$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_3$ after calcination at 1250 °C. Left: $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_3$. Right: from back to front $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_3$, $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_3$, $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_3$.



Figure A.2: 40g samples of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_3$ and $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_3$ after calcination at 1300 °C, Left: $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_3$, Right: $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_3$.

A.2 Powder XRD Diffractograms

A.2.1 5 g batches

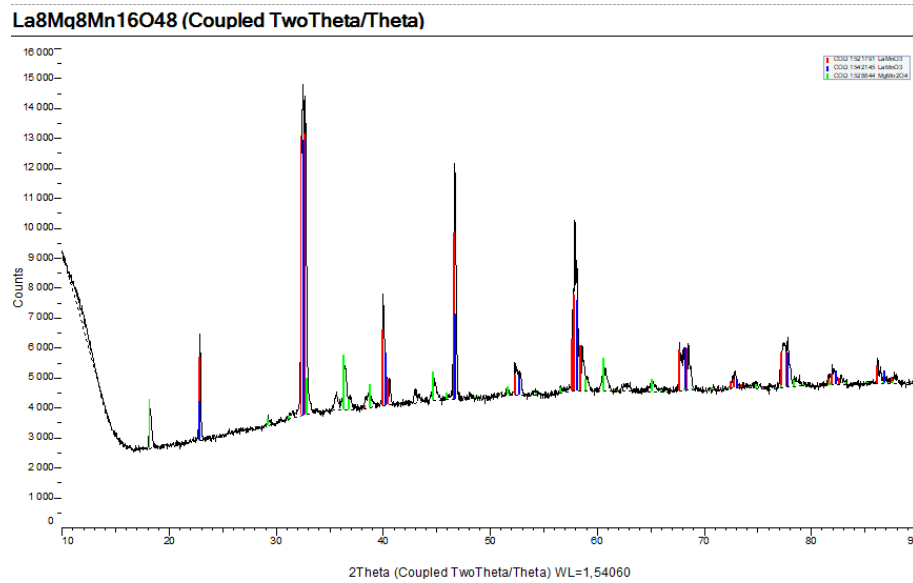


Figure A.3: Diffractogram of the small batch of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

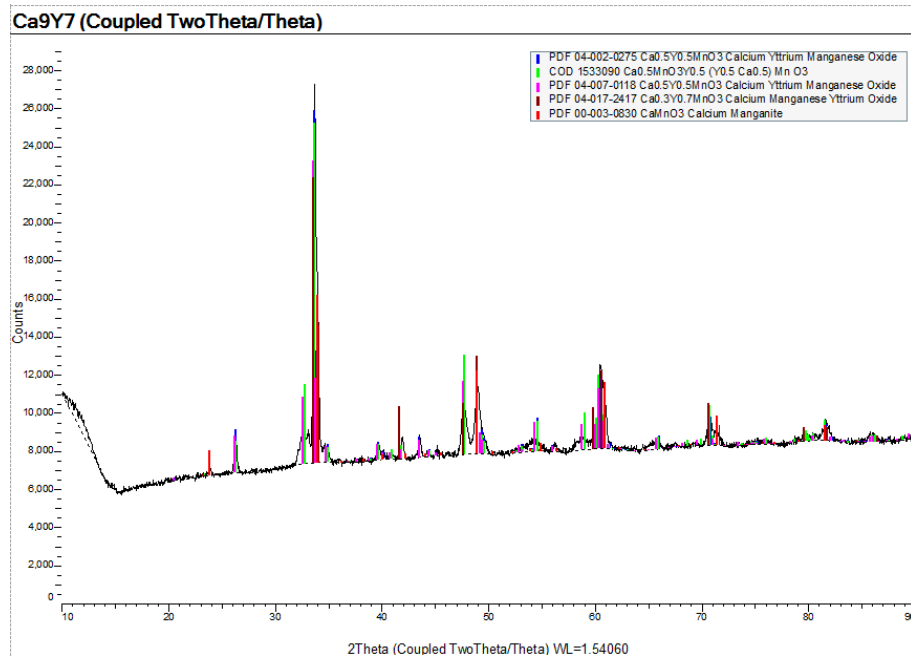


Figure A.4: Diffractogram of the small batch of $\text{Ca}_{0.56}\text{Y}_{0.44}\text{MnO}_{3-\delta}$.

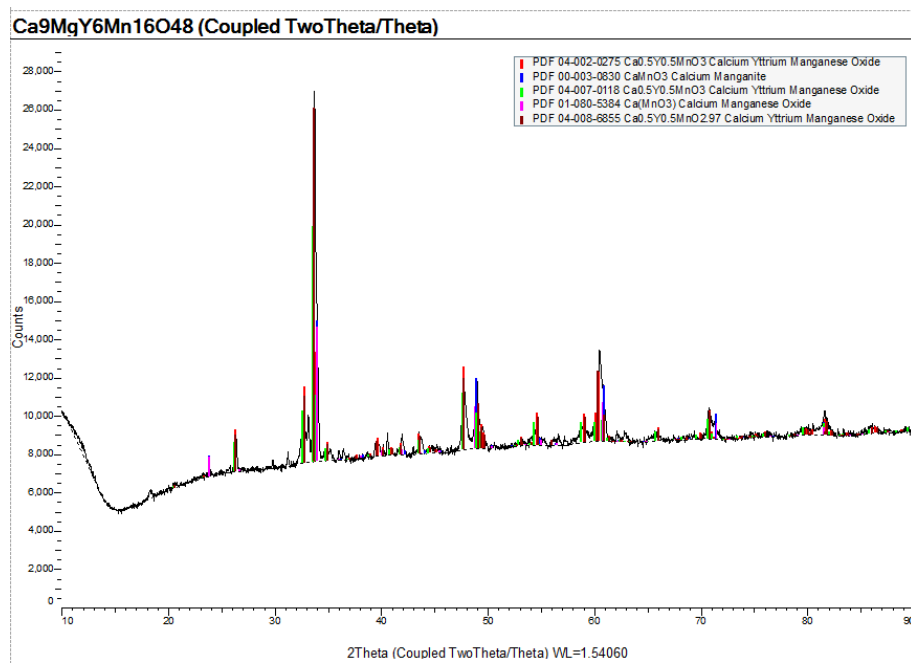


Figure A.5: Diffractogram of the small batch of $\text{Ca}_{0.56}\text{Mg}_{0.063}\text{Y}_{0.38}\text{MnO}_{3-\delta}$.

A.2.2 Large batches

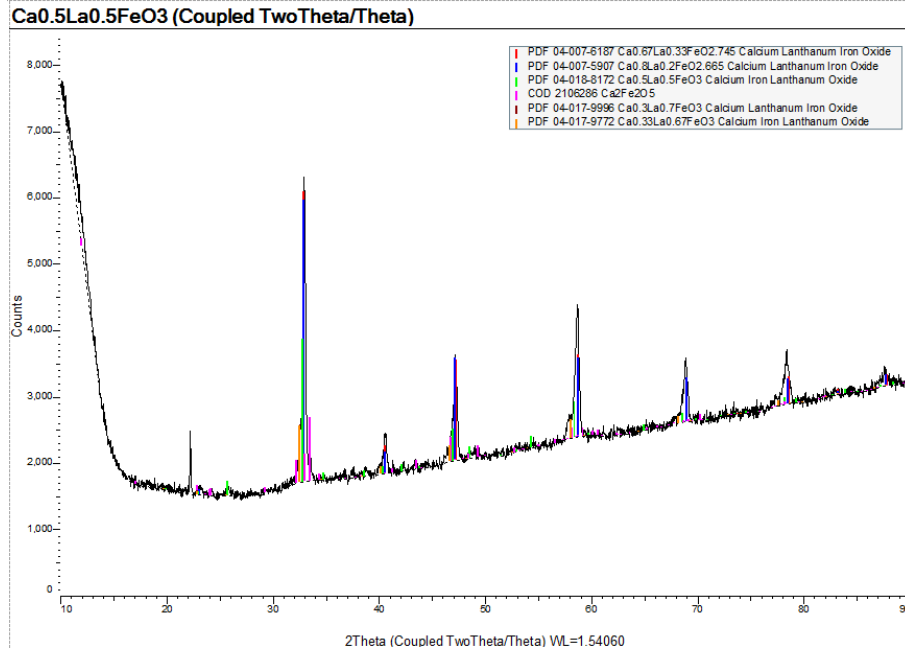


Figure A.6: Diffractogram of the large batch of $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$.

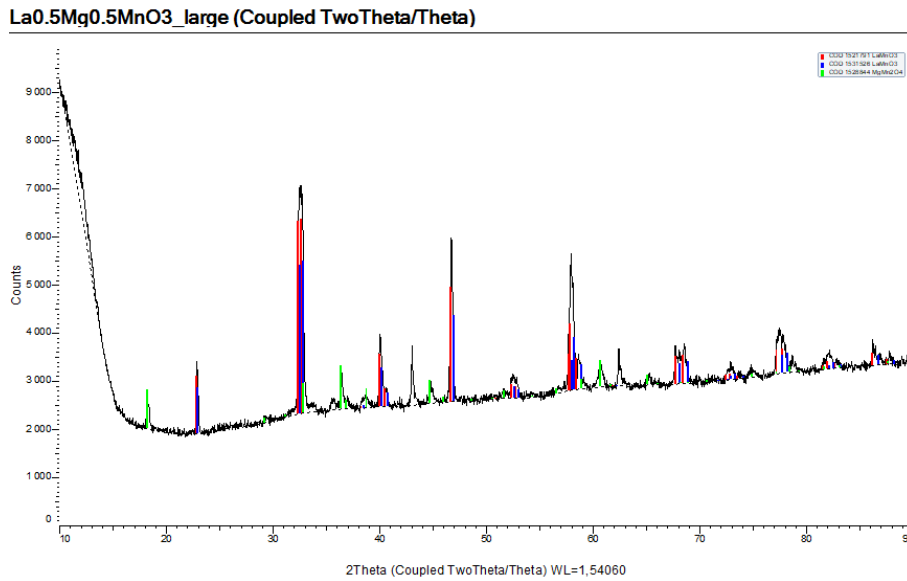


Figure A.7: Diffractogram of the large batch of $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ calcined at 1300 °C, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

A.3 EDS analyses

A.3.0.1 Fresh $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$

Table A.1: Elemental composition data, fresh $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, light phase 1.

Element Name	Atomic Concentration [%]
Lanthanum	51.9
Oxygen	27.0
Manganese	16.5
Magnesium	4.7

Table A.2: Elemental composition data, fresh $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, light phase 2.

Element Name	Atomic Concentration [%]
Lanthanum	35.3
Oxygen	43.2
Manganese	13.7
Magnesium	7.8

Table A.3: Elemental composition data, fresh $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, light phase 3.

Element Name	Atomic Concentration [%]
Lanthanum	32.2
Oxygen	45.4
Manganese	18.1
Magnesium	4.4

Table A.4: Elemental composition data, fresh $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, dark phase 1.

Element Name	Atomic Concentration [%]
Lanthanum	4.3
Oxygen	55.9
Manganese	21.2
Magnesium	18.7

Table A.5: Elemental composition data, fresh $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, dark phase 2.

Element Name	Atomic Concentration [%]
Lanthanum	19.0
Oxygen	41.4
Manganese	26.0
Magnesium	13.7

Table A.6: Elemental composition data, fresh $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, shadow.

Element Name	Atomic Concentration [%]
Lanthanum	53.5
Manganese	30.0
Magnesium	16.5

A.3.0.2 Used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$

Table A.7: Elemental composition data, used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, light phase 1.

Element Name	Atomic Concentration [%]
Lanthanum	32.2
Oxygen	48.8
Manganese	12.4
Magnesium	6.6

Table A.8: Elemental composition data, used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, light phase 2.

Element Name	Atomic Concentration [%]
Lanthanum	49.5
Oxygen	27.9
Manganese	16.3
Magnesium	6.4

Table A.9: Elemental composition data, used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, light phase 3.

Element Name	Atomic Concentration [%]
Lanthanum	36.4
Oxygen	35.3
Manganese	18.1
Magnesium	10.2

Table A.10: Elemental composition data, used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, dark phase 1.

Element Name	Atomic Concentration [%]
Lanthanum	1.9
Oxygen	57.4
Manganese	24.6
Magnesium	16.1

Table A.11: Elemental composition data, used $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, dark phase 2.

Element Name	Atomic Concentration [%]
Lanthanum	1.7
Oxygen	55.5
Manganese	26.6
Magnesium	16.3

Table A.12: Elemental composition data, fresh $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$, dark phase 3.

Element Name	Atomic Concentration [%]
Lanthanum	7.1
Oxygen	37.2
Manganese	55.7
Magnesium	0

A.4 CLWS experiments

A.4.1 $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$

Table A.13: List of SR experiments performed with $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$ after deflu-idisation including the cycle number and SR temperature, The FR time was 60 s for all experiments.

Cycle	T_{SR} [°C]
18	900
19	900
20	800
21	700
22	800
23	700
24	800
25	700

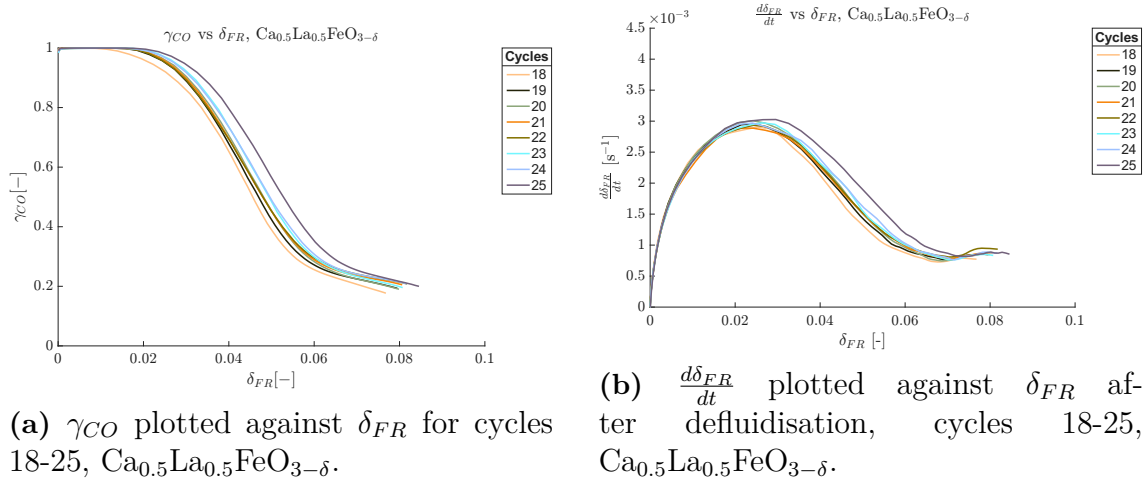


Figure A.8: γ_{CO} and $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 18-25, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$.

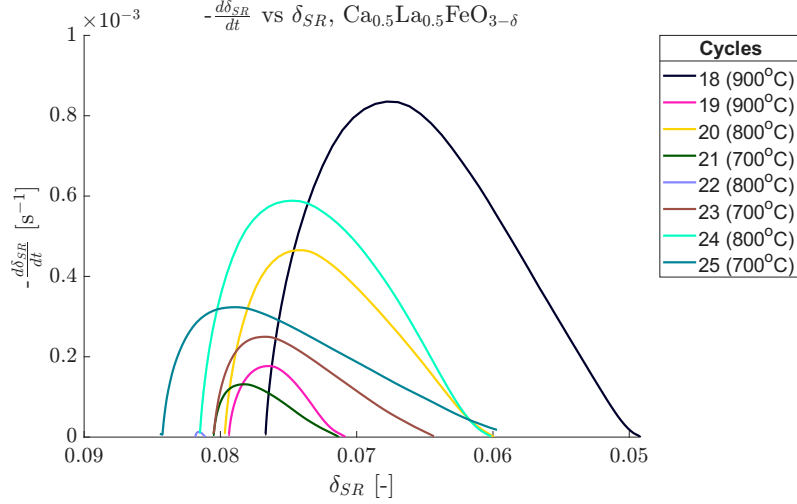
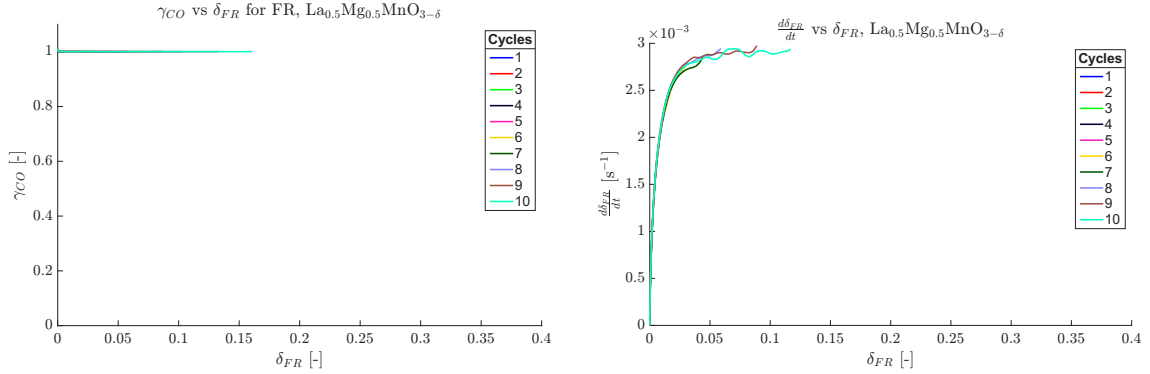
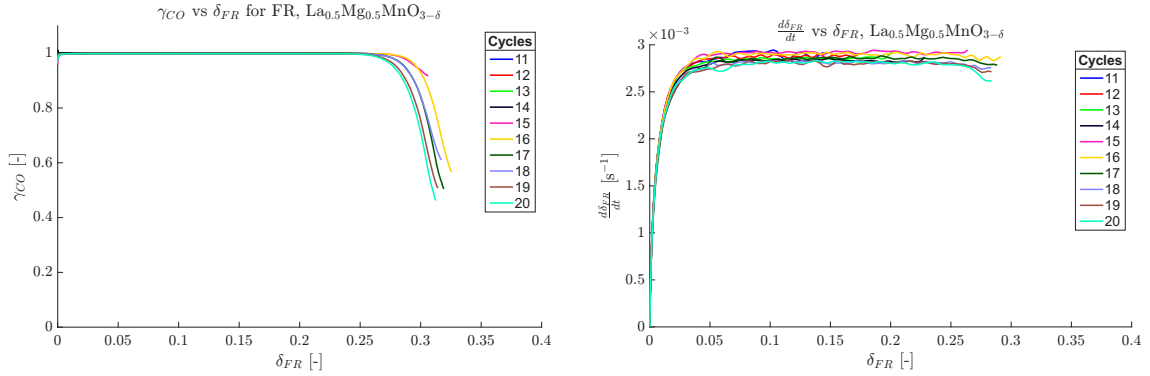
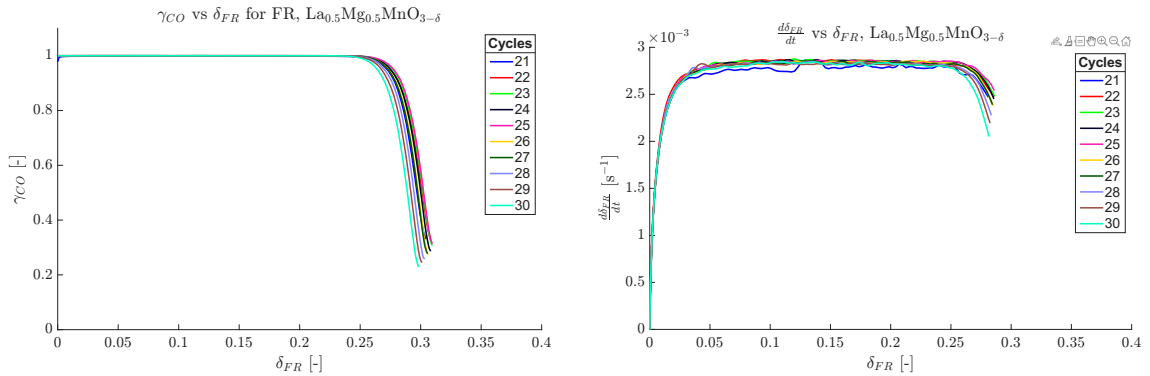
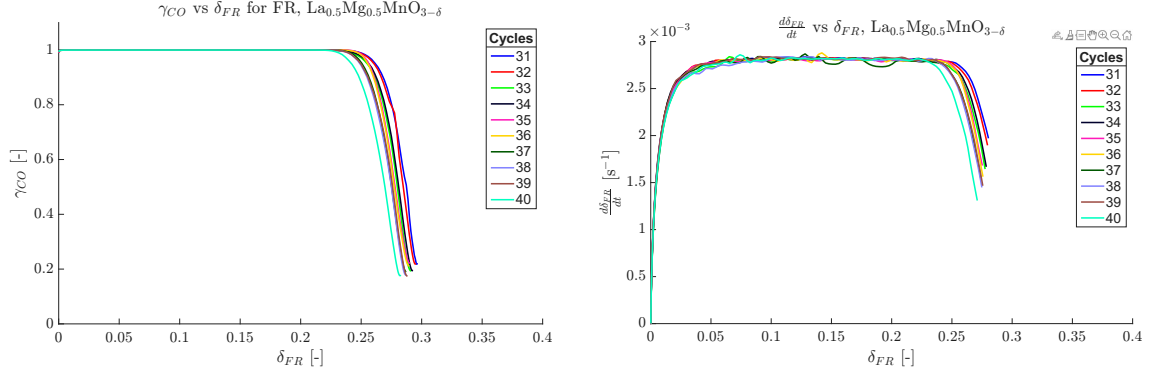


Figure A.9: $-\frac{d\delta_{SR}}{dt}$ plotted against δ_{SR} after defluidisation, $\text{Ca}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$.

A.4.2 $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ (a) γ_{CO} plotted against δ_{FR} for cycles 1-10, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.(b) $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 1-10, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.**Figure A.10:** γ_{CO} and $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 1-10, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.(a) γ_{CO} plotted against δ_{FR} for cycles 11-20, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.(b) $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 11-20, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.**Figure A.11:** γ_{CO} and $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 11-20, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.(a) γ_{CO} plotted against δ_{FR} for cycles 21-30, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.(b) $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 21-30, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.**Figure A.12:** γ_{CO} and $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 21-30, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

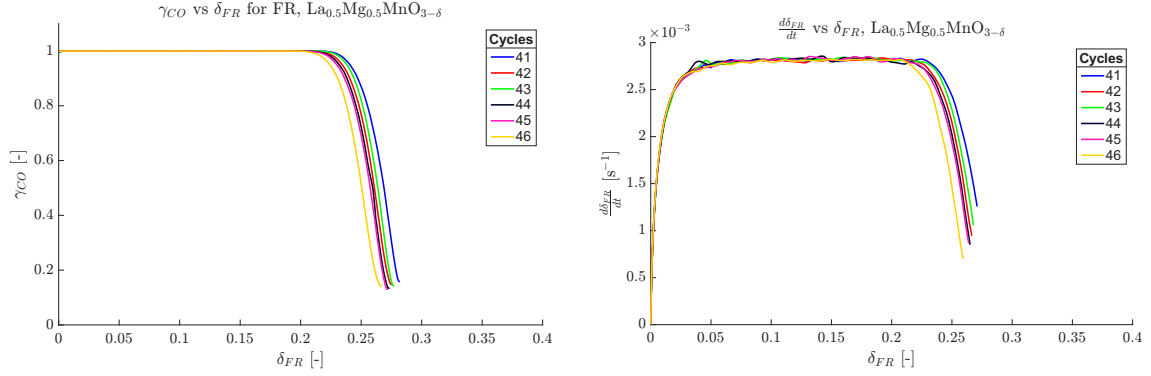
A. Appendix



(a) γ_{CO} plotted against δ_{FR} for cycles 31-40, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

(b) $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 31-40, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

Figure A.13: γ_{CO} and $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 31-40, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.



(a) γ_{CO} plotted against δ_{FR} for cycles 41-46, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

(b) $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 41-46, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

Figure A.14: γ_{CO} and $\frac{d\delta_{FR}}{dt}$ plotted against δ_{FR} for cycles 41-46, $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$.

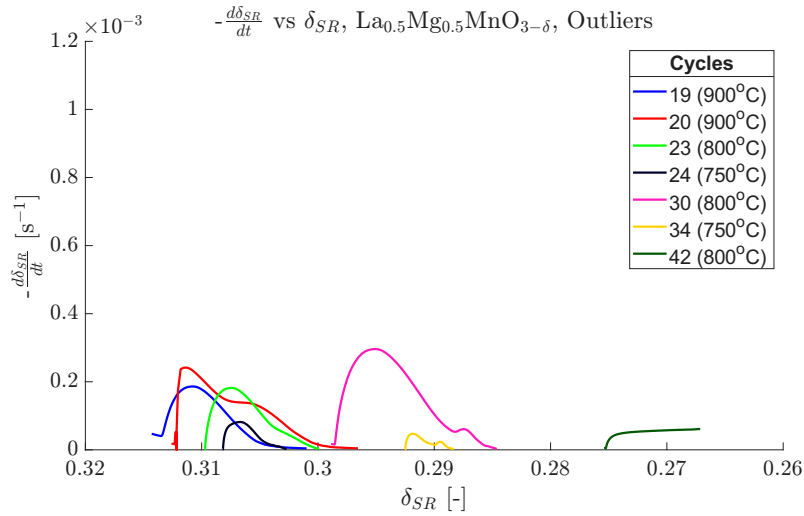


Figure A.15: $-\frac{d\delta_{SR}}{dt}$ plotted against δ_{SR} , $\text{La}_{0.5}\text{Mg}_{0.5}\text{MnO}_{3-\delta}$ outliers.

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