



MASTER THESIS

Electrochemical properties of $LiMn_2O_4$ as electrode on oxygen ion conducting ZrO_2

carried out for the purpose of obtaining the degree of

Master of Science

submitted at TU Wien, Faculty of Physics, by

Felix Oblak

Matr.Nr.: 11702369

under the supervision of

Univ.Prof. Dipl.-Phys. Dr.rer.nat Jürgen Fleig and

Ass.Prof. Dipl.-Ing. Dr.rer.nat Markus Kubicek Institute of Chemical Technologies and Analytics, E164 I confirm, that going to press of this thesis needs the conformation of the examination committee.

Affidavit

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. If text passages from sources are used literally, they are marked as such.

I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it currently under consideration for a thesis elsewhere.

Vienna on December 7, 2024

file Olik

Signature

Felix Oblak

Abstract

Providing clean and sustainable energy is a central challenge in contemporary energy economics. Renewable energy sources, relying on intermittent factors such as sunlight and wind, require efficient storage solutions. Batteries and fuel cells are essential to ensure a stable and continuous green energy supply.

This study initiates a link between electrochemical cells based on lithium and oxygen by examining LiMn_2O_4 (LMO), a commonly used lithium-ion battery material, towards effects of oxygen stoichiometry and its impact on structural stability. LMO was deposited as thin film onto yttria-stabilized zirconia (YSZ), a high-performance oxygen ion conductor used in solid oxide fuel cells, to analyse the electrochemical properties and stability of LMO in this configuration.

Using X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS), the change of oxygen content supposedly enabled via oxygen vacancies in LMO under various conditions were assessed. In situ XRD revealed initial lattice expansion in oxygen atmospheres, with contraction around 550 °C due to oxygen release, and thermal expansion above 750 °C. Under nitrogen, phase transitions occurred above 700 °C. Based on these data, the temperature range for impedance spectroscopic measurements was chosen to avoid phase transitions at low oxygen partial pressures.

EIS data indicated that the chemical capacitance of LMO thin films increased while the resistance decreased with increasing temperature, due to increased defect (e.g. oxygen vacancy) concentrations. Lower oxygen partial pressures correlated with higher capacitance, especially at elevated temperatures. While the capacitance behaviour remained consistent across all lithium contents, delithiated samples exhibited significantly steeper gradients in the logarithmic plots of capacitance versus oxygen partial pressure, attributed to lower capacitance at high oxygen partial pressures. The resistance remained largely stable, except at higher temperatures with low oxygen partial pressures. After reaching the maximum temperature and minimum oxygen partial pressure in the EIS measurements, the lithium content of the thin films can still be circulated. The material exhibits highly stable behaviour across various lithium concentrations throughout the temperature cycle, as well as under different oxygen partial pressures.

Kurzfassung

Die Bereitstellung sauberer und nachhaltiger Energie stellt eine zentrale Herausforderung in der modernen Energiewirtschaft dar. Erneuerbare Energiequellen, die von variierenden Umweltfaktoren wie Sonneneinstrahlung und Wind abhängig sind, erfordern effiziente Speicherlösungen. Batterien und Brennstoffzellen sind essenziell, um eine stabile und kontinuierliche Versorgung mit grüner Energie sicherzustellen.

Diese Studie schlägt eine Brücke zwischen elektrochemischen Zellen basierend auf Lithium und Sauerstoff, indem sie LiMn_2O_4 (LMO), ein häufig verwendetes Lithium-Ionen-Batteriematerial, auf die Auswirkungen der Sauerstoffstöchiometrie und deren Einfluss auf die strukturelle Stabilität untersucht. Zu diesem Zweck wurde LMO als Dünnschicht auf Yttrium-stabilisiertes Zirkoniumoxid (YSZ), einem leistungsstarken Sauerstoff-Ionen-Leiter, abgeschieden, der häufig in Festoxidbrennstoffzellen Anwendung findet, um die elektrochemischen Eigenschaften und Stabilität von LMO in dieser Konfiguration zu analysieren.

Die Veränderung des Sauerstoffgehalts in LMO, vermutlich hervorgerufen durch Sauerstoffleerstellen unter verschiedenen Bedingungen, wurde mithilfe von Röntgendiffraktometrie (XRD) und elektrochemischer Impedanzspektroskopie (EIS) analysiert. Die in-situ-XRD-Messungen zeigten eine anfängliche Gitterexpansion in Sauerstoffatmosphäre, eine Kontraktion bei etwa 550 °C aufgrund von Sauerstofffreisetzung sowie eine thermische Expansion über 750 °C. In Stickstoffatmosphäre traten Phasenübergänge bei Temperaturen über 700 °C auf. Basierend auf diesen Daten wurde die Temperatur bei den impedanzspektroskopischen Messungen begrenzt, um Phasenübergänge bei niedrigen Sauerstoffpartialdrücken zu vermeiden.

Die EIS-Daten zeigten, dass die chemische Kapazität der LMO-Dünnschicht mit steigender Temperatur zunahm, während der Widerstand aufgrund der erhöhten Konzentration an Defekten wie z.B. Sauerstoffleerstellen abnahm. Niedrigere Sauerstoffpartialdrücke korrelierten mit höheren Kapazitäten, insbesondere bei erhöhten Temperaturen. Während dieses Kapazitätsverhalten über alle Lithiumgehälter hinweg konsistent blieb, zeigten delithiierte Proben deutlich höhere Gradienten in logarithmischen Auftragungen der Kapazität gegen den Sauerstoffpartialdruck, was auf geringere Kapazitäten bei hohen Sauerstoffpartialdrücken zurückzuführen ist. Der Widerstand blieb überwiegend stabil, mit Ausnahme eines Anstiegs bei höheren Temperaturen und niedrigen Sauerstoffpartialdrücken. Die Ergebnisse deuten darauf hin, dass der Lithiumgehalt nach den EIS-Messungen weitgehend zirkulierbar bleibt, obwohl Nebenreaktionen im Elektrolyten eine präzise Vergleichbarkeit der Ladezyklen einschränken. Das Material zeigt ein sehr stabiles Verhalten bei verschiedenen Lithiumgehältern über den betrachteten Temperaturzyklus sowie bei unterschiedlichen Sauerstoffpartialdrücken.

Contents

1 Indroduction	1
2 Theoretical background	4
2.1 Defect chemistry	4
2.2 Vacancies, chemical potential, and chemical capacitance	6
2.2.1 Chemical potential and chemical capacitance	6
2.2.2 Vacancies and chemical capacitance	7
2.2.3 Interplay between vacancies, chemical potential, and chemical capacitance	7
2.3 Crystal structure and defect chemistry of LMO	8
2.3.1 Crystal structure of LMO	8
2.3.2 Defects in spinel-type oxides	9
2.3.3 Defect chemistry of LMO during the state of charge (SOC)	9
2.4 Electrochemical impedance spectroscopy (EIS)	10
2.4.1 Experimental setup	11
2.4.2 Nyquist and Bode plots	11
2.4.3 Components in equivalent circuit models	12
3 Experimental section	15
3.1 Sample preparation	15
3.1.1 YSZ single crytals	15
3.1.2 Platinum current collector	16
3.1.3 RF magnetron sputtering of LMO layers	16
3.1.4 Delithiation process	17
3.2 Material characterization	17
3.2.1 X-ray diffraction (XRD)	17
3.2.2 Scanning electron microscopy (SEM)	18
3.2.3 Inductively coupled plasma optical emission spectroscopy (ICP-OES)	18
3.3 Electrical characterization	18
3.3.1 Measurement setup	18
3.3.2 Experimental workflow	20
3.3.3 Data analysis	21

CONTENTS

4 Results and discussion	23								
4.1 In situ X-ray diffraction	23								
4.1.1 In situ XRD in oxygen atmosphere	24								
4.1.2 In situ XRD in nitrogen atmosphere \ldots	26								
4.1.3 In situ XRD analysis of delithiated LMO	27								
4.2 SEM measurements	29								
4.3 Electrochemical impedance spectroscopy (EIS)	32								
4.3.1 Models	32								
4.3.2 Variation of the temperature	38								
4.3.3 Variation of the oxygen partial pressure	43								
4.3.4 Variation of the lithium content	49								
4.4 Circulation capability	70								
5 Conclusions									
A Directories 7									
A.1 List of Illustrations	74								
A.2 List of Tables	77								
A.3 Bibliography	78								

Chapter 1

Indroduction

Providing clean and sustainable energy represents one of the foremost challenges within contemporary energy economics. Due to the intermittent nature of renewable energy sources relying on variables such as sunlight and wind speed — efficient energy storage technologies are essential. Batteries and fuel cells play a key role in this context, contributing significantly to the stabilisation and continuous supply of green energy in various applications [1,2].

Within this context, two different scientific areas are established the "Lithium World" and the "Oxygen World" to describe the distinct mechanisms and materials central to modern energy storage systems, such as lithium-ion batteries (LIBs) and solid oxide fuel cells (SOFCs). These "Worlds" are characterized by specific chemical properties and challenges that are essential for the efficiency and longevity of these energy storage technologies.

The "Lithium World" refers to energy storage systems that utilize lithium ions as charge carriers, such as LIBs. In LIBs, the insertion and extraction of lithium ions between the anode and cathode constitute the primary electrochemical processes enabling reversible energy storage and release with a high energy density. During charging, lithium ions migrate from the cathode through the electrolyte to the anode, where they are intercalated into the layers of the anode material, typically graphite. Simultaneously, electrons flow from the external power source to the anode, facilitating energy storage. During discharge, this process reverses: lithium ions move back from the anode to the cathode, while electrons flow through the external circuit, delivering electrical energy. Although theoretically reversible, these cycles gradually lead to capacity losses due to material degradation and side reactions [3]. Commonly used cathode materials such as lithium cobalt oxide [4, 5], lithium iron phosphate [6, 7], and lithium manganese oxide [8–13] each exhibit distinct properties in terms of stability and performance:

 \rightarrow Lithium cobalt oxide (LiCoO₂): Known for its high energy density, LiCoO₂ is widely used in portable electronics, such as smartphones and laptops. Its layered structure enables efficient lithium ion movement, contributing to excellent energy storage capacity. However, $LiCoO_2$ has moderate thermal stability and can become unstable at high temperatures, presenting safety risks under extreme conditions or if overcharged. Additionally, its reliance on cobalt, which has ethical and environmental concerns, and high production costs make it less suitable for applications where long-term stability and lower costs are essential, such as electric vehicles.

- → Lithium iron phosphate (LiFePO₄): LiFePO₄ is celebrated for its superior thermal stability and safety, as it is less prone to overheating and thermal runaway than LiCoO₂. Its excellent cycle life and stability under high current loads make it particularly suitable for applications requiring safety and longevity, such as electric vehicles and stationary energy storage systems. However, it has a lower energy density compared to LiCoO₂, which limits its use in applications where compact energy storage is a priority. LiFePO₄ is also advantageous due to its reliance on more abundant and environmentally friendly materials, enhancing its appeal in sustainable energy solutions.
- → Lithium manganese oxide (LiMn₂O₄): Known for its high thermal stability and low cost, LMO offers a balance between performance, safety, and affordability. Its spinel structure enables three-dimensional lithium ion movement, improving ion transport and making it suitable for high-power applications. LiMn₂O₄ has a moderate energy density, making it a strong candidate for both portable electrical devices and larger applications such as electric vehicles. However, it is prone to capacity fading over extended cycling due to the dissolution of manganese in the electrolyte, especially at elevated temperatures. Researchers are exploring dopants and coating techniques to enhance its long-term stability and performance.

Despite their success in mobile applications and stationary energy storage, lithium-based systems face challenges such as material stability, safety concerns, and limited raw material supply, which increasingly necessitate research and technological development [14, 15].

In contrast, the "Oxygen World" encompasses energy storage systems that employ oxygen ions as charge carriers, such as solid oxide fuel cells (SOFCs) and oxygen batteries. These systems, typically operating at high temperatures, rely on ion-conducting ceramics like yttria-stabilized zirconia (YSZ), known for its high oxygen ion conductivity and stability in both oxidizing and reducing conditions [16]. SOFCs use oxygen ions as charge carriers and are recognized for their efficiency in stationary energy applications. Operating at temperatures between 600 and 1000 °C, SOFCs consist of a cathode, an anode, and a solid electrolyte [17]. At the cathode, oxygen molecules are reduced to oxygen ions, which migrate through the electrolyte to the anode. At the anode, these oxygen ions react with a fuel, such as hydrogen or natural gas, producing water (and carbon dioxide in the case of hydrocarbons) and releasing electrons, which flow through an external circuit to generate electricity. Additional materials like lanthanum strontium manganite (LSM) [18] and lanthanum strontium cobaltite (LSC) [19] are commonly used in SOFC cathodes, providing high thermal stability and efficient oxygen ion uptake and transport. SOFCs offer versatility in fuel choice and high efficiency, making them well-suited for applications in combined heat and power systems and industrial settings [20]. However, the high operating temperatures introduce thermal stresses on components and increase production costs, which challenge durability and commercial viability. Research efforts are directed at developing more durable materials and reducing operating temperatures to improve longevity and economic feasibility [21].

In summary, the "Lithium World" and "Oxygen World" offer distinct but complementary approaches to energy storage and conversion. Lithium-ion batteries are well-suited for mobile applications due to their high energy density and low operating temperatures, whereas solid oxide fuel cells are ideal for stationary applications that prioritize efficiency and fuel versatility. The development of advanced, durable materials in both domains remains a critical focus of research and interstingly, despite many of the relevant materials are complex oxides that are chemically similar, there is limited scientific overlap between the respective communities. The highest overlap, so far, is given by the following two facts: At the annealing temperature of LIB cathode materials, the interaction with the oxygen in the gas phase may affect the capacitance [22]. And overcharging or thermal runaways may lead to the loss of oxygen in the cathode with highly detrimental consequences [23–25].

This study takes an initial step toward establishing a further link between the lithium and oxygen domains by examining the behaviour of LiMn_2O_4 (LMO), a material commonly used in lithium-ion batteries, with respect to oxygen release and the resulting effects on its structural and functional properties. In this investigation, LMO is deposited via RF magnetron sputtering [26,27] onto YSZ. The primary objective of this research is to conduct an in-depth investigation into the behaviour of oxygen stoichiometry in LMO as a function of temperature, oxygen partial pressure and lithium content. This includes a characterization of the stability and electrochemical properties of the material. An experimental methodology is employed, incorporating in situ X-ray diffraction (XRD) measurements and electrochemical impedance spectroscopy (EIS) to monitor structural and electrical changes in LMO under various external conditions.

Chapter 2

Theoretical background

In the following chapter, key theories essential to this research will be discussed. The chapter begins with an examination of the fundamental principles of defect chemistry, which will later be applied to the LMO under study. This includes a detailed description of the LMO's crystal structure and its charge state. The subsequent section will delve into electrochemical impedance spectroscopy, where the basic concepts will be outlined. Additionally, the various components necessary for the analysis and interpretation of the later modelling work will be explained in detail.

2.1 Defect chemistry

The structure of crystalline solids is described using the unit cell. This cell contains all the structural and symmetry information of a crystal and represents the smallest repeating unit that, through translation in all spatial directions, builds the ideal macroscopic crystal.

Point defects: In this context, all regular lattice sites of the crystal lattice are occupied by the corresponding atoms or ions. However, in all real crystals, deviations from the ideal structure occur. Concerning elementary conduction mechanisms, zero-dimensional defects, known as point defects, are crucial. Point defects are local disturbances in the periodic arrangement of atoms in a crystal lattice. They are classified into several types:

- $\rightarrow\,$ Vacancies: Missing atoms in the lattice.
- $\rightarrow\,$ Interstitials: Atoms that occupy positions between the regular lattice sites.
- \rightarrow Substitutional Defects: Atoms of one element replacing atoms of another element in the lattice.

In Figure 2.1, the various types of point defects are illustrated.



Figure 2.1: Classification of point defects.

Kröger-Vink notation is a systematic method used in materials science and solid-state chemistry to describe point defects and defect reactions in crystalline materials. It provides a standardized way to represent the types, concentrations, and behaviours of defects.

Particles can be any atoms or vacancies (V...vacancy). Possible sites include regular lattice sites or interstitial sites (i...interstitial). The relative charge is the difference between the actual charge and the ideal charge. Positive values are indicated with ".",negative with "!". If the relative charge is zero, " \times " is used.

The presence of structural defects often leads to electronic "defects" due to the necessity of charge neutrality. These are denoted as e' for an extra electron or h^{\cdot} for a hole. Using this notation, the extraction of lithium from the cathode of a lithium-ion battery can be represented as:

$$nil \Leftrightarrow Li + V'_{Li} + h^{\cdot} \tag{2.1}$$

Alternatively, the formation of oxygen vacancies can be described by the following expression:

$$\frac{1}{2}O_2 + 2e' + V_O^{"} \Leftrightarrow O_O^{\times}$$
(2.2)

Point defects facilitate the migration of ions within the crystal lattice. Ions "jump" from one lattice site to a vacancy or an interstitial site, and this process occurs continuously in all directions at finite temperatures. When there are driving forces such as concentration gradients and/or external electric fields, there is a preferential migration in one direction, resulting in a net transport of matter and charge. There are essentially three main causes for point defects:

- 1. Intrinsic defects due to thermodynamic reasons.
- 2. Extrinsic defects caused by impurities or intentional doping.
- 3. Defects resulting from deviations in stoichiometry.

These defects influence the electrical, optical, and mechanical properties of materials by altering their atomic structure and electronic environment.

2.2 Vacancies, chemical potential, and chemical capacitance

Vacancies, chemical potential, and chemical capacitance are closely interrelated concepts that play a fundamental role in materials science, electrochemistry, and solid-state chemistry. Vacancies, as point defects within a crystal lattice, facilitate the redistribution of species within a material, significantly influencing its chemical behaviour. The chemical potential represents the collective energy ensemble of a species, such as particles or defects, and determines how their concentration changes in response to energy variations. The chemical capacitance quantifies a material's ability to adjust the concentration of such species in response to changes in chemical potential.

2.2.1 Chemical potential and chemical capacitance

Chemical potential, denoted by μ , is a fundamental thermodynamic parameter representing the change in free energy of a system when the number of particles changes at constant temperature and pressure. It plays a vital role in determining the direction of chemical reactions and phase changes [28]. The chemical capacitance of a material describes its ability to change the concentration of a neutral species such as "O" or "Li" with a change in the species' chemical potential. It can be determined using the chemical potential as follows:

$$C_{Chem} = q^2 V \left(\frac{\partial \mu_i}{\partial c_i}\right)^{-1} \tag{2.3}$$

where V is the sample volume, q is the elementary charge, μ_i is the chemical potential of the atomic species, and c_i is the concentration of formally neutral atoms, i.e., Li⁺ along with its corresponding electron.

- \rightarrow **Driving force for reactions:** The chemical potential serves as the driving force for diffusion and chemical reactions. In a system where there is a gradient in chemical potential, particles (such as atoms, ions, or molecules) move from regions of higher chemical potential to regions of lower chemical potential. This movement can create or annihilate vacancies, thus impacting the chemical capacitance of the system.
- \rightarrow Relation to vacancies: The formation energy of vacancies is related to the chemical potential of the constituent atoms or ions. For example, the chemical potential of oxygen in an oxide material influences the concentration of oxygen vacancies. Lower oxygen chemical potential (e.g., in a reducing environment) leads to the formation of more oxygen vacancies, altering the material's capacitance for oxidation and reduction reactions.

 \rightarrow Phase equilibria and capacitance: The chemical potential determines the phase behaviour of a material. At equilibrium, the chemical potential of a species is the same across all phases. Variations in chemical potential, driven by external factors such as temperature, pressure, or composition, can lead to phase transitions that affect the material's chemical capacitance. For instance, in battery materials, changes in chemical potential during charging and discharging cycles can lead to phase transformations that either enhance or diminish the material's capacitance.

2.2.2 Vacancies and chemical capacitance

In crystalline solids, vacancies are empty lattice sites resulting from the absence of an atom or ion that would normally occupy that position. These vacancies can significantly influence the material's chemical capacitance, especially in ionic conductors, semiconductors, and battery materials.

- → Ion mobility: Vacancies facilitate the movement of ions within a solid. For example, in a lithium-ion battery, lithium vacancies in the electrode material (such as LiMn_2O_4) allow lithium ions to move in and out of the lattice during charge and discharge cycles. The number and distribution of vacancies directly impact the material's ability to accommodate and release lithium ions, thereby influencing the battery's capacitance.
- \rightarrow Redox reactions: Vacancies can also affect the redox behaviour of materials. In transition metal oxides used in batteries, for instance, oxygen vacancies can influence the oxidation state of the metal ions, altering the material's redox capacity. A higher concentration of vacancies might enhance the material's ability to undergo redox reactions, thus increasing its chemical capacitance.
- \rightarrow Thermodynamic stability: The formation of vacancies is related to the thermodynamic stability of a material. At high temperatures or under certain chemical environments, the vacancy concentration can increase, affecting both the material's phase stability and its chemical capacitance. For example, in solid oxide fuel cells, oxygen vacancies are critical for ionic conductivity, which is crucial for the device's efficiency.

2.2.3 Interplay between vacancies, chemical potential, and chemical capacitance

The interplay between vacancies and chemical potential directly correlates with a material's chemical capacitance:

→ Vacancy formation and chemical potential: The formation of vacancies depends on the chemical potential of the involved species. A higher chemical potential of a component (e.g. oxygen in this study) makes the formation of vacancies less favorable, while a lower chemical potential makes vacancy formation more favorable. This balance affects how many particles a material can accommodate, thus influencing its chemical capacitance.

- \rightarrow Capacitance and diffusion: Since vacancies enhance ionic or atomic diffusion by providing pathways for movement, and chemical potential gradients drive this diffusion, the overall capacitance of a system to undergo chemical changes (such as concentration variation due to ion intercalation in batteries) is dictated by both vacancy concentration and chemical potential.
- → Thermodynamic limits: The chemical potential sets thermodynamic limits on the maximum capacitance of a material. When the chemical potential of the intercalating ion (e.g., lithium) becomes too low, further intercalation becomes energetically unfavorable, limiting the capacitance. Similarly, too many vacancies can destabilize the lattice, leading to structural collapse and a reduction in capacitance.

In summary, understanding and controlling the relationship between vacancies and chemical potential is key to optimizing the chemical capacitance of advanced materials. This correlation plays a crucial role in applications such as energy storage, catalysis, and materials science, where maximizing chemical capacitance is essential for performance improvement.

2.3 Crystal structure and defect chemistry of LMO

Lithium manganese oxide $(\text{LiMn}_2\text{O}_4)$, commonly referred to as LMO, is a prominent material in battery technology due to its promising electrochemical properties, making it an excellent candidate for use in lithium-ion batteries. The focus of this chapter is to explore the crystal structure and defect chemistry of LMO, emphasizing their impact on the material's electrochemical performance and stability. As a cathode material, LMO grown in a spinel structure is used, providing several advantages, including high voltage operation, good thermal stability, and cost-effectiveness [29].

2.3.1 Crystal structure of LMO

 $LiMn_2O_4$ crystallizes in the cubic spinel structure with the space group Fd3m shown in Figure 2.2. In this structure, lithium ions occupy the tetrahedral 8a sites, while manganese and oxygen ions are located in the octahedral 16d and 32e sites, respectively [30]. The general formula for a spinel is AB₂O₄, where A ions occupy tetrahedral sites and B ions occupy octahedral sites. For LiMn₂O₄:

- \rightarrow A site: Li^+
- \rightarrow B site: Mn^{3+} and Mn^{4+}

The oxygen ions form a close-packed cubic sublattice, while the lithium and manganese ions occupy the interstitial sites.



Figure 2.2: Crytal structure of $LiMn_2O_4$.

The high symmetry of the cubic spinel structure facilitates the diffusion of lithium ions during charge and discharge cycles. The spinel structure provides three-dimensional pathways for lithium-ion diffusion, contributing to high ionic conductivity and rate capability [29].

2.3.2 Defects in spinel-type oxides

Spinel-type oxides, such as LiMn_2O_4 , are commonly used as cathode materials in lithium-ion batteries due to their favourable electrochemical properties. Defects in these materials play a crucial role in determining their performance. The removal of lithium ions from the lattice (delithiation) can lead to the formation of vacancies, which can affect the structural stability and ionic conductivity of the material. The incorporation of excess lithium ions can lead to interstitial defects, which may alter the electrochemical behaviour and stability of the material [31].

2.3.3 Defect chemistry of LMO during the state of charge (SOC)

The oxidation of Mn^{3+} to Mn^{4+} in $Li_{2-\delta}Mn_2O_4$ ($\delta > 1$) results in the release of Li⁺ ions from the tetrahedral 8a sites. By the discharging of the tetrahedral 8a sites the behaviour of the two different regimes is shown in a characteristic double plateau in the charge curve, occurring at approximately 4.00 and 4.15 V versus Li⁺/Li [27].

The first plateau corresponds to a single-phase solid solution within the composition range of $\text{Li}_{2-\delta}\text{Mn}_2\text{O}_4$ ($\delta > 1$), extending up to the non-stoichiometric limit of $\delta = 1.5$. At this stage, the remaining Li ions reorganize to minimize electrostatic repulsion, stabilizing the occupied 8a sites relative to those that are vacant. Electrostatic repulsion refers to the repulsive interaction

between the positively charged lithium ions. The system arranges the remaining lithium ions in a manner that minimizes these repulsive interactions, thus stabilizing the crystal structure at $\delta = 1.5$. During this process, a gradual reduction in the cubic lattice parameter from the initial 8.24 Å to 8.19 Å is observed [27, 30]. Consequently, further delithiation from these occupied Li sites occurs at a higher electrode potential, resulting in a sudden decrease in the lattice parameter to 8.14 Å. In Li_{0.5}Mn₂O₄, the equivalent 8a sites are split in one fully occupied site and the other vacant. The second plateau, ranging from $\delta = 1.5$ to $\delta = 2.0$, with a significantly flatter potential profile compared to the first plateau, is associated with a first-order phase transition from a Li-rich $\delta \approx 1.65$ to a Li-poor $\delta \approx 1.9$ phase. The discharging process can be described by the following formula:

$$Li_1 M n_1^{3+} M n_1^{4+} O_4 \to Li_0 M n_2^{4+} O_4$$
 (2.4)

The electrochemical lithium storage in LMO can be divided into three distinct regimes:

- 1. Lithium ions are stored at octahedral 16d sites for δ values in the range $0 \leq \delta \leq 1$,
- 2. disordered lithium storage occurs at tetrahedral 8a sites for $1 \leq \delta \leq 1.5$, and
- 3. ordered lithium storage is observed at tetrahedral 8a sites for $1.5 \leq \delta \leq 2$ [27].

2.4 Electrochemical impedance spectroscopy (EIS)

Impedance spectroscopy, particularly electrochemical impedance spectroscopy (EIS), is an essential technique for probing the electrical properties of electrochemical systems. This section explores the theoretical foundations, methodologies, and applications of EIS in electrochemical measurements, with an emphasis on batteries, fuel cells and electrode kinetics.

EIS is an alternating current technique that serves as a crucial tool in solid-state electrochemistry. During a measurement, a low-amplitude sinusoidal alternating voltage (10 mV) is applied to the sample via two contacts. The sample responds to this input signal with an output signal in the form of a sinusoidal alternating current of the same frequency. The analytical information is derived from the ratio of the amplitudes and the phase shift between the input and output signals. This information is encapsulated in the complex, frequency-dependent quantity known as impedance (Z). The real part of impedance provides information about the amplitude ratios, indicating energy dissipation in the system, while the imaginary part provides information about the phase shift, indicating energy storage in the system. The impedance (Z) is defined as the complex ratio of the voltage response (V) to the applied current (I).

$$Z(\omega) = \frac{V(\omega)}{I(\omega)}$$
(2.5)

where ω is the angular frequency of the AC signal. Impedance comprises a real part (resistance, R) and an imaginary part (reactance, X):

$$Z(\omega) = R(\omega) + jX(\omega)$$
(2.6)

j is the imaginary unit. The frequency range typically extends from 10^{-3} Hz to 10^{7} Hz, depending on the processes and materials under investigation. For specific applications requiring measurements at very low frequencies in the mHz range, extended measurement times — often lasting several hours — are necessary, emphasizing the importance of system stability. The very low currents typically used during measurements ensure that the surfaces under examination remain virtually unaltered.

An equivalent circuit is a conceptual model composed of ideal circuit elements that replicates the electrical behaviour of the actual object under examination. The specific configuration is determined through theoretical considerations of potential (electrochemical) processes within the system and supplementary analytical data. This is essential because, from a purely mathematical standpoint, multiple equivalent circuits can represent a single measured impedance spectrum. The quantitative parameters of the individual impedance elements are derived by mathematically fitting them to the frequency response of the measured spectrum. These parameters reflect the electrical properties of the real processes occurring within the system. A thorough understanding of the system enables the creation of an equivalent circuit diagram, allowing changes in electrical behaviour to be interpreted as alterations in individual system components. This method is particularly effective for studying electrochemical systems such as batteries and fuel cells.

2.4.1 Experimental setup

An EIS experiment typically involves the following components:

- $\rightarrow\,$ Signal Generator: Applies the AC signal across the electrochemical cell.
- \rightarrow Potentiostat/Galvanostat: Controls the potential or current applied to the electrochemical cell.
- \rightarrow Frequency Response Analyser (FRA): Measures the system's response.
- \rightarrow Electrochemical Cell: The system under study, which can be a battery, fuel cell, or in the case of this study an electrode.

2.4.2 Nyquist and Bode plots

In a Nyquist plot, the imaginary component of impedance $(X(\omega))$ is plotted against the real component $(R(\omega))$. This plot is particularly useful for visualizing processes such as charge transfer resistance and double-layer capacitance and is predominantly used in this work to visualize impedance results. Bode plot represents the magnitude of the impedance and the phase angle as functions of frequency. This helps in understanding how the impedance varies with frequency, highlighting different electrochemical processes.

2.4.3 Components in equivalent circuit models

Resistor (R): Represents the resistance in the system, such as the charge transfer resistance, the ion resistance through the electrolyte or the oxygen insertion/extraction resistance at the electrode.

$$Z_R = R \tag{2.7}$$

The resistance is frequency-independent and is solely determined by the amplitude ratios of the measured signals.

Capacitor (C): Models the capacitive behaviour, like the double-layer capacitance at an electrode interface or the chemical capacitance. A capacitor introduces a phase difference of $-\pi/2$ between voltage and current.

$$Z_C(\omega) = \frac{1}{j\omega C} \tag{2.8}$$

Inductor (L): Occasionally used to model inductive behaviours, though less common in electrochemical systems. An inductor introduces a phase difference of $+\pi/2$ between voltage and current. These components will not be considered further, as they play a secondary role in the system being analysed.

$$Z_L(\omega) = j\omega L \tag{2.9}$$

Constant Phase Element (CPE): The CPE is a mathematical construct used to describe the impedance of a system that exhibits frequency-dependent behaviour which deviates from ideal capacitive or resistive behaviour. It is particularly useful for modelling systems with surface inhomogeneities, roughness, or other non-idealities.

$$Z_{CPE}(\omega) = \frac{1}{(Q(j\omega)^n)}$$
(2.10)

 $n: 0 \leq n \leq 1$

- \rightarrow When n = 1: The CPE behaves like an ideal capacitor. The impedance follows $Z_{CPE} = 1/j\omega C$, where C is the capacitance.
- \rightarrow When n = 0: The CPE behaves like a pure resistor. The impedance is $Z_{CPE} = 1/R$, where R is the resistance.

 \rightarrow When 0 < n < 1: The CPE represents a more complex behaviour between ideal capacitance and resistance, modelling systems with distributed resistance or capacitance. In this case, the impedance shows a phase angle that varies with frequency. For values of n near 1, Q is interpreted as a non-ideal capacitance. In this case, Q can be converted into units of an actual capacitance using the following Equation [32].

$$C = \left(R^{1-n}Q\right)^{1/n} \tag{2.11}$$

Warburg Impedance (W): Represents diffusion-controlled processes, either semi-infinite or finite diffusion. The semi-infinite Warburg element describes the diffusion impedance in an unbounded or semi-infinite medium, where the diffusion length is much smaller than the system dimensions, effectively assuming an infinite medium for diffusion. The impedance of the semi-infinite Warburg element is given by:

$$Z_W(\omega) = \sigma\left(\frac{1-j}{\sqrt{\omega}}\right) \tag{2.12}$$

Where σ is the Warburg coefficient, ω is the angular frequency, and j is the imaginary unit. The semi-infinite Warburg (W_I) impedance shows a characteristic $\sqrt{\omega}$ dependence, where the impedance decreases with the square root of the frequency. In a Nyquist plot, the semi-infinite Warburg element appears as a straight line with a 45-degree slope at low frequencies, indicating the square root relationship between impedance and frequency [33].



Figure 2.3: Charateristics of the different Warburg elements; semi-infinite Warburg W_I , open Warburg W_o and closed Warburg W_s .

For finite diffusion processes, two distinct elements can be discussed: the Open Warburg element and the Closed Warburg element. The open Warburg element (W_o) represents finite-length diffusion with a reflective boundary and is expressed by the following equation:

$$Z_{W_o}(\omega) = R_{ion} \cdot (j\omega\tau)^{-1/2} \cdot \coth(j\omega\tau)^{1/2}$$
(2.13)

where R_{ion} is the ionic resistance, ω is the angular frequency, j is the imaginary unit, and τ is the characteristic time constant related to the diffusion process. The impedance of the Open Warburg element decreases with $\sqrt{\omega}$ at low frequencies, approximates resistive behaviour at high frequencies, and transitions between these behaviours at intermediate frequencies. Shows a characteristic shape with a semicircle at intermediate frequencies and a 45-degree line at low frequencies, reflecting the mixed resistive and capacitive nature of the impedance due to finitelength diffusion with reflective boundaries. This element is used in scenarios where ions or electrons diffuse within a thin film that has reflective boundaries at its interfaces, such as the diffusion of lithium ions through a cathode.

The closed Warburg element (W_s) , on the other hand, characterizes the impedance of a finitelength diffusion with a transmissive boundary and is expressed by the following equation:

$$Z_{W_s}(\omega) = R_{ion} \cdot (j\omega\tau)^{-1/2} \cdot tanh (j\omega\tau)^{1/2}$$
(2.14)

At high frequencies, the finite Warburg impedance behaves similarly to a purely resistive element, while at low frequencies, it transitions towards a capacitive behaviour. In a Nyquist plot, the finite Warburg element typically shows a depressed semicircle or a straight line transitioning into a semicircle, indicating the finite diffusion effects [34, 35].

In this thesis, a model incorporating a closed Warburg element of finite length is employed to describe the transmission of oxygen vacancies through the active LMO thin layer. This model is explained in detail in subsection 3.3.3.

Chapter 3

Experimental section

3.1 Sample preparation

Figure 3.1 presents the structure of the samples utilized in this study. The subsequent section provides a detailed description of the fabrication process for each individual component of the samples.



Figure 3.1: Layer composition of the applied symmetrical sample geometry.

3.1.1 YSZ single crytals

The samples under investigation exhibit a symmetrical configuration. A double-sided polished yttrium-stabilized zirconium dioxide single crystal (Mateck, Germany), hereinafter referred to as YSZ, is employed as the substrate. The YSZ substrate has an (100) orientation and dimensions of $5 \text{ mm} \times 5 \text{ mm} \times 0.5 \text{ mm}$. YSZ is a ceramic material known for its high ionic conductivity at elevated temperatures. Due to its exclusive conduction of oxygen ions, it is widely used as an electrolyte material in solid oxide fuel cells and in lambda sensors. Initially, the YSZ crystal was subjected to a thorough cleaning process. The substrates were sonicated for 10 min each in a 3% aqueous solution of extran, bidistilled water, and ethanol.

3.1.2 Platinum current collector

To establish an electronic contact for measurement purposes, a platinum grid with a titanium interlayer was used as the current collector on the single crystal. This was achieved through DC sputtering at room temperature under an argon atmosphere of 0.7/2.5 Pa, employing a current density of 5 mA/cm^2 to deposit a 5 nm layer of titanium followed by a 100 nm layer of platinum.

Using lithographic techniques, a grid pattern with $15 \times 15 \,\mu\text{m}^2$ squares and $5 \,\mu\text{m}$ grid was manufactured on the Pt layer, and the grid structure was created using an ion beam etcher. To achieve the grid pattern, photoresist was deposited on the sample and evenly distributed using a spin coater, followed by heating at 100 °C for 4 min. The sample was then exposed to UV light for 30 s using a negative mask containing the corresponding grid pattern. The development time was approximately 2.5 to 3.5 min. The developed surfaces were then available for subsequent etching.

The etching process was carried out in an ion beam etcher (tectra GmbH, ionEtch Sputter Gun), with the chamber evacuated to a pressure in the low 10^{-6} mbar range. Argon was used as the working gas, and a pressure of 90 mPa was established. The ion beam etching process is conducted with a voltage of 400 V and a beam current of 15 mA. The etching duration, determined using dummy samples (YSZ crystals (100) with 5/100 nm of Ti/Pt), ranged from 12 to 14 min. The process was then applied to both sides of the sample. Finally, the photoresist was removed by cleaning the sample with ethanol.

3.1.3 RF magnetron sputtering of LMO layers

The LiMn₂O₄ layer to be analysed was deposited on both sides on the YSZ single crystal with the current collectors using radio-frequency (RF) magnetron sputtering. The sputtering was carried out in a custom-built deposition chamber (Huber Scientific, Austria). The chamber was evacuated to a pressure in the low 10^{-5} mbar range. The 2" diameter LMO sputtering target was supplied by ALB Materials, USA. The LMO was deposited with a process pressure of 2.5 Pa (comprising 25% O_2 and 75% Ar), at a substrate-to-target distance of 6.0 cm and a power of 60 W. A power-temperature calibration conducted on a YSZ (100) single crystal (CrysTec, Germany) with dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 0.5 \text{ mm}$ was used to determine the nominal substrate temperature on the heating stage, which was set for the process to 550 °C. An optical pyrometer was used for calibration, with a preset surface emissivity coefficient of $\varepsilon = 0.9$. After a processing time of 1.5 hours, the average thickness of the LMO layer was determined to be approximately 80 nm, as measured by TEM. This corresponds to a deposition rate of 0.89 nm/min [27].

3.1.4 Delithiation process

For the delithiation process, the samples were placed in a cell containing an aqueous electrolyte. The cell consisted of a working electrode, which was the sample itself, an aqueous electrolyte of 1 M LiNiO_3 , and a counter electrode made of platinum. An Ag/AgCl electrode was used as the reference electrode. Platinum wires served as electrode contacts, resulting in only partial sample contact and a longer electron pathway due to in-plane conduction within the LMO layer. Furthermore, potential imperfections in the sample's contact may reduce the proportion of the total lithium content that is cyclable.

The cell was cycled with a rate of 1 mV/s multiple times using a BioLogic SP-200 potentiostat (with EIS) to ensure stable operation. Subsequently, the cells were discharged to a specific voltage, indicating the removal of a certain amount of Li-ions from the cathode. The process was analysed using BioLogic EC-Lab software. These delithed samples will later be analysed using impedance spectroscopy to establish a correlation between their chemical properties and their state of charge. The lithium content of the sample will be estimated from the discharge curve. A more precise definition of the lithium content is obtained through ICP-OES measurements, as re-incorporation of lithium ions can occur.

After the delithiation process was completed, the sides of the sample were sanded down to ensure there were no short circuits at the edges. The sample was then ready for analysis using impedance spectroscopy.

3.2 Material characterization

3.2.1 X-ray diffraction (XRD)

The LMO thin films were analysed via X-ray diffraction using an empyrean multipurpose diffractometer (Luthien; Malvern Panalytical, Germany). Theta-2-theta scans were recorded before and after the electrochemical measurements were applied to the sample. A Cu anode was used, with an operating voltage of 45 kV and a tube current of 40 mA.

Additionally, in situ measurements were conducted using the Empyrean multipurpose diffractometer (Legolas; Malvern Panalytical, Germany). As with the previous measurements, a Cu anode with an operating voltage of 45 kV and a tube current of 40 mA was used. These measurements were carried out under nitrogen and oxygen atmospheres, both gases supplied by Messer Austria GmbH. The samples were examined over a temperature range from $25 \,^{\circ}\text{C}$ to $1200 \,^{\circ}\text{C}$ in 25 K increments to investigate phase transitions in the LMO layers.

3.2.2 Scanning electron microscopy (SEM)

SEM operates on the principle of scanning a focused electron beam over the surface of a sample, resulting in the generation of high-resolution images and detailed structural information. Unlike optical microscopes, SEM uses electrons instead of light, allowing for much higher magnification and resolution. In addition, the surface of the samples was examined using scanning electron microscopy (SEM) to analyse the structural properties of the LMO layers. The SEM images were acquired using the FEI Quanta 250 at the USTEM facility of TU Wien.

3.2.3 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was employed to characterize the samples with regard to their lithium and manganese stoichiometry. This analysis was essential for accurately determining the state of charge of the LMO thin films, particularly to assess the extent of delithiation. ICP-OES is well-known for its high sensitivity, precision, and capability to simultaneously analyse multiple elements. The technique utilizes inductively coupled plasma to excite atoms and ions, causing them to emit light at specific wavelengths. The emitted light is then measured to determine the elemental concentrations in the sample.

The measurements were conducted using an Agilent 5110 ICP-OES, with quantification achieved through external calibration using matrix-matched standards. Samples are typically introduced into the ICP-OES system in the form of an aerosol; therefore, the solid LMO film layers were dissolved in 0.5 mL of concentrated HCl (36 wt % HCl in H₂O, Merck EMSURE for trace analysis) and heated to 90 °C for 30 minutes. The solution was then diluted to 10 mL with Milli-Q water, and europium was added as an internal standard (1 ppm Eu in solution). This procedure resulted in lithium and manganese concentrations of approximately 0.1 to 0.5 ppm, which are ideal for accurate measurements. Consequently, the samples are destroyed during the analysis and cannot be reused.

3.3 Electrical characterization

3.3.1 Measurement setup

The measurement setup included a sample holder mounted into a threaded flange, equipped with a Type K thermocouple for temperature measurement. To achieve a defined gas atmosphere, a quartz tube was placed over the sample holder and secured to the flange. The overall setup featured a quartz sample holder, an outer fused silica tube, a tube furnace, a PID controller, and mass flow controllers with a control unit. Figure 3.2 provides a detailed view of the setup and Figure 3.3 is highlighting the sample holder with the thermocouple. Experimental Conditions: All experiments were conducted in specified O_2 - N_2 mixtures (both gases are supplied by Messer Austria GmbH with a purity of 99.999%) and 1% O_2 (supplied by Air Liquide Austria GmbH). The gas flow was regulated by two mass flow controllers (MFCs) connected to a controller unit. The sample heating was performed using a tube furnace, with the furnace temperature managed by an Eurotherm PID Controller connected to the furnace. For impedance measurements, a Novocontrol Alpha-A High Performance Frequency Analyzer with an Electrochemical Test Station POT/GAL 30 V/2 A was utilized. The control of the devices and data acquisition were managed using a customized software.



Figure 3.2: EIS measurement setup: a) quartz sample holder, b) outer fused silica tube, c) tube furnace, d) mass flow controllers with control unit, e) gas inlet and outlet, f) thermocouple, g) grounding



Figure 3.3: Detailed view of the sample holder used for the EIS measurement: (a) quartz sample holder, (f) thermocouple, (h) Pt contacts

3.3.2 Experimental workflow

The workflow was consistent for all samples. Initially, the sample was placed in the sample holder. The fused silica tube was carefully slid over the sample holder, and the outer tube was screwed to the flange. To ensure there was no short circuit, the setup was tested with a multimeter. The tube furnace, mounted on sliding rails, was then slid over the quartz outer tube. The gas flow was controlled to achieve the desired partial oxygen pressure using two mass flow controllers (MFCs): one for N₂ and the other for O₂ and the 1% O₂/N₂ mixture, with a three-way valve to switch between the gases.

The initial temperature of the furnace was set via the customized software Elchitools. To establish a stable atmosphere, the setup was allowed to equilibrate for at least three hours before starting the measurements. For the impedance spectroscopy measurements, a Novocontrol Alpha-A High Performance Frequency Analyzer with an Electrochemical Test Station 30 V/2 A was used. The measurements employed a four-point probe method, involving four separate probes to make electrical contact with the material. The two outer probes sourced current, while the two inner probes measured the voltage drop, minimizing the effect of contact resistance and providing a more accurate measurement of electrical impedance.

Variation of temperature: The measuring probe was placed inside a furnace to achieve the desired measurement temperatures, ranging from $400 \,^{\circ}$ C to $650 \,^{\circ}$ C in steps of 50 K. The sample temperature, determined using a Type K thermocouple, was approximately 30 K lower than the corresponding furnace set temperature.

Variation of oxygen partial pressure: Impedance spectroscopy was conducted under specific atmospheres with varying oxygen partial pressures and temperatures. The variation of oxygen partial pressure was controlled using MFCs, which regulated the ratios of O_2 , 1% O_2 , and N_2 . The Table 3.1 summarizes the partial pressures and their corresponding gas flows. The gas mixtures were continuously directed over the measuring probe, ensuring direct contact with the cathode.

Table 3.1 :	List	of oxygen	partial	pressure	p_{O_2}	and	their	corresponding	$O_2,$	N_2	and	1%	O_2	flow
rates.														

p_{O_2}	[mbar]	1000	500	200	100	50	20
O_2	[sccm]	33.0	33.0	33.0	16.5	8.7	3.3
N_2	[sccm]	0.0	33.0	132.0	148.5	165.0	161.7
p_{O_2}	[mbar]	10	5	2	1	0.5	0.2
$1\% O_2$	[sccm]	33.0	33.0	33.0	16.5	8.7	3.3
N_2	[sccm]	0.0	33.0	132.0	148.5	165.0	161.7

An AC signal with a range of frequencies was applied to the cell. During data acquisition, the voltage and current responses were measured and recorded. Subsequently, the collected data was analysed to obtain the impedance spectrum.

3.3.3 Data analysis

Equivalent circuit models, composed of resistors, capacitors, constant phase elements and Warburg elements, are used to interpret EIS data. These models correlate the measured impedance with the physical and electrochemical phenomena occurring within the system. The data analysis is fitted to an equivalent circuit model using the software tool ZView 4. The fitting process helps in extracting meaningful parameters such as resistance, capacitance, and diffusion coefficients. Error analysis involves assessing the goodness-of-fit and calculating confidence intervals for the fitted parameters. This ensures the reliability and accuracy of the derived electrochemical properties. Interpreting EIS data involves correlating the features of Nyquist and Bode plots with specific electrochemical processes. For instance, a semicircle in the Nyquist plot usually indicates charge transfer resistance, while a linear segment at low frequencies suggests diffusion control.

In this study, several fitting models were applied and compared. Initially, a resistance model was used for the YSZ single crystal, combined with an R-CPE (Constant Phase Element) circuit in series to determine the capacitance and resistance of the active LMO layer, to be seen in Figure 3.4. Since the impedance spectrum did not form an ideal semicircle, the fitting was performed using a CPE.



Figure 3.4: Model 1: YSZ resistance in series with one R-CPE element.

The second model involved two R-CPE elements in series (seen in Figure 3.5) to better match the data being fitted. However, this model does not always clarify whether the capacitance represent the chemical capacitance of the active LMO layer, which is influenced by oxygen insertion and extraction.



Figure 3.5: Model 2: YSZ resistance in series with two R-CPE elements.

In addition to the models, a transmission line model (TLM) was employed to achieve a clearer attribution of the individual capacitances and resistances shown in the Figure 3.6. This model includes a series resistance for the YSZ crystal and a closed Warburg element with an ideal capacitor in parallel. The Warburg element describes the ionic bulk resistance of the LMO layer and, through its period, allows for the determination of the chemical capacitance. The parallel capacitor represents the electronic coupling within the ionic conduction path.



Figure 3.6: Model 3: Transmission line model with no surface resistance.

Chapter 4

Results and discussion

In this chapter, the experimental findings of the study will be presented and analysed in detail. The discussion will begin with the results obtained from the in-situ X-ray diffraction (XRD) measurements, providing insights into the structural evolution of the LMO thin films under varying temperature and atmospheric conditions. Following this, the scanning electron microscopy (SEM) images will be examined to evaluate the surface morphology and microstructural changes of the samples.

The second part of the chapter will focus on the interpretation of the impedance spectroscopy measurements. Here, the relationships between key electrochemical parameters such as resistances, capacitances, and their dependence on temperature, oxygen partial pressure, and the lithium content of the material will be explored. Particular emphasis will be placed on how these factors influence the overall electrochemical performance of the LMO thin films and contribute to a deeper understanding of oxygen non-stoichiometry behaviour within the system. These analyses will lay the groundwork for identifying the underlying mechanisms governing the material's stability and performance under the examined experimental conditions.

4.1 In situ X-ray diffraction

In this section, the results of the in-situ X-ray diffraction (XRD) measurements are discussed in detail. These measurements were carried out under controlled nitrogen and oxygen atmospheres, allowing for a thorough investigation of the material's structural changes in response to varying environmental conditions. Diffraction patterns were recorded over a temperature range from $25 \,^{\circ}$ C (room temperature) to $1200 \,^{\circ}$ C, in $25 \,^{\circ}$ K intervals. These measurements provide insights into phase transitions, lattice expansions due to thermal expansion, and oxygen release. The findings regarding the material's stability under these conditions will be used in the subsequent impedance spectroscopy analysis to prevent irreversible changes in the LMO thin films.

For the measurements of non-delithiated LMO, single-side polished YSZ crystals (100) with dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 0.5 \text{ mm}$ (CrysTec, Germany) were used and coated with an LMO layer of 160 nm thickness. The sputtering process was executed in accordance with the methodology detailed in subsection 3.1.3. For the analysis of delithiated LMO, the samples were prepared following the established protocol presented in section 3.1.

4.1.1 In situ XRD in oxygen atmosphere

Figure 4.1 illustrates the diffraction patterns recorded at various temperatures within an oxygen atmosphere. Notably, for temperatures below 500 °C, a gradual shift of the LMO peaks towards lower angles is observed with increasing temperature.



Figure 4.1: X-ray diffraction patterns of LMO recorded at various temperatures under an oxygen atmosphere, including the position of the two peaks considered from the literature [36].

For better visualization, Figure 4.2 illustrates the evolution of the (111) (left) and (222) (right) reflexes over the temperature range. The measurements performed in an oxygen atmosphere are represented by the black curves.

Up to approximately 500 °C, the peaks shift to smaller angles, followed by a shift toward higher angles, reaching a maximum at 750 °C, close to the initial peak values. Afterwards, the peaks shift again to lower angles. The lattice parameters were determined from the individual peaks according to Bragg's law

$$n\lambda = 2d_{hkl}\sin\left(\theta\right) \tag{4.1}$$

where n is the order of diffraction, λ is the wavelength of the incident wave, d_{hkl} is the spacing between crystal planes, and θ is the angle of incidence. The variation of the lattice parameter over the temperature range for both reflexes is shown in Figure 4.3. The behaviour in the oxygen atmosphere is illustrated in black. For the (111) peak, Bragg's law indicates a lattice



Figure 4.2: Displacement of the (111) peak (left) and the (222) peak (right) of the LMO under nitrogen and oxygen atmosphere, across the temperature range from 25 °C to 1200 °C.

expansion of the LiMn_2O_4 thin film from 8.16 Å to 8.20 Å, with the thermal expansion reaching a maximum at 500 °C. This lattice parameter is lower than the expected value of 8.24 Å at room temperature [27]. One possible explanation for this discrepancy is a higher lithium content in this sample, as ICP-OES measurements indicate an overall higher lithium concentration in the samples [37]. Another possible explanation is a systematic error in the measurement setup, which could account for the discrepancy observed in the lattice parameter calculated from the (222) peaks.



Figure 4.3: Variations of the lattice parameter of LMO under nitrogen and oxygen atmosphere determined from the (111) peak (left) and the (222) peak (right) measured in the temperature range from $25 \,^{\circ}$ C to $1200 \,^{\circ}$ C.

Between 500 °C and 750 °C, the lattice parameter decreases, likely due to oxygen release from the LiMn_2O_4 thin film. Above 750 °C, the lattice parameter increases again, with a significant peak shift attributed to enhanced thermal expansion of the lattice. At the upper end of the temperature range, at 1200 °C, the lattice spacing reaches 8.48 Å, and the expansion begins to plateau. This flattening may indicate lithium loss into the atmosphere, which is expected to occur above a certain temperature threshold for high lithium contents.

The (222) peak shows similar results, though the lattice parameter at 25 °C is higher, measuring 8.22 Å. The lattice expansion continues up to 500 °C, where the parameter reaches 8.26 Å according to Bragg's law. The reduction in lattice size due to oxygen release is also evident for this peak. At high temperatures, the behaviour mirrors that of the (111) peak, with reduced thermal expansion below 500 °C and a renewed increase in expansion above 1000 °C. The plateauing effect from the possible lithium extraction is as well observed. The lattice spacing for the (222) peak is higher at 8.54 Å compared to the (111) peak. The increase in lattice spacing remains consistent, with a difference of approximately 0.06 Å, suggesting a potential systematic error in the XRD measurements.

4.1.2 In situ XRD in nitrogen atmosphere

Figure 4.4 presents the diffraction patterns obtained at different temperatures under a nitrogen atmosphere.



Figure 4.4: X-ray diffractions of LMO at different temperatures in an nitrogen atmosphere, including the position of the two peaks considered from the literature [36].

In Figure 4.3, the two analysed peaks under nitrogen atmosphere are illustrated in green. The behaviour observed between $25 \,^{\circ}$ C and $500 \,^{\circ}$ C is largely consistent with that under oxygen, except for a slight shift of approximately $0.03 \,^{\circ}$ A towards larger lattice spacings. The expected oxygen release is evident, as indicated by the decreasing lattice parameters. Above $550 \,^{\circ}$ C, the formation of two parallel phases becomes apparent, continuing up to $700 \,^{\circ}$ C. At this tempera-

ture, the LMO peaks disappear, leaving only the newly formed Mn_3O_4 phase shown in red. This new phase is identified as Mn_3O_4 , and the phase transition can be described by the following reaction:

$$3 \operatorname{LiMn}_2 O_4 \to \operatorname{Mn}_3 O_4 + 3 \operatorname{LiMn}_2 + O_2$$

$$(4.2)$$

This phase transition has been previously reported in the literature and is confirmed in this study [38,39]. The behaviour observed at higher temperatures likely indicates additional phase transitions, contributing to the reduction in lattice parameters.

A second study highlighted, through thermogravimetric analysis (TGA) measurements at high temperatures up to $1200 \,^{\circ}$ C, the occurrence of certain phase transitions. The temperatures at which the first of these phase transitions occur shift from $902 \,^{\circ}$ C in an atmosphere of $100 \,\%$ oxygen to $714 \,^{\circ}$ C in an atmosphere with $0 \,\%$ oxygen [40]. In a nitrogen atmosphere, the phase transition is also observed at approximately $700 \,^{\circ}$ C, confirming this transition measured via the in situ XRD-measurements. However, in an oxygen atmosphere, no phase transition is evident around $900 \,^{\circ}$ C. According to the paper, additional phase transitions are expected to occur at $836 \,^{\circ}$ C and $1060 \,^{\circ}$ C in an atmosphere with $0 \,\%$ oxygen. The first transition is not clearly identifiable in Figure 4.3, while the second transition, occurring around $1060 \,^{\circ}$ C, is observable only for the (222) peak. A second phase transition is anticipated at $1005 \,^{\circ}$ C in an atmosphere with $100 \,\%$ oxygen [40]. At this temperature, there is at least an increase in the slope of the lattice parameter, which could be indicative of a phase transition.

In the case of the (222) peak, the lattice parameters at lower temperatures in a nitrogen atmosphere are very similar to those observed in an oxygen atmosphere. The phase transition is also clearly visible in the (222) peak. At 1000 °C the formation of a new peak is observed near the (222) peak, indicating the appearance of a new phase. The value of this peak decreases with increasing temperature. Up to 1100 °C both peaks can be observed simultaneously, but beyond this temperature neither peak remains detectable.

Based on these results, the maximum sample temperature in subsequent experiments was limited to below $625 \,^{\circ}\text{C}$ to prevent further irreversible phase transitions.

4.1.3 In situ XRD analysis of delithiated LMO

In addition to the two over-lithiated samples, two delithiated samples were analysed. These samples were discharged at a potential of 1 V with respect to the Ag/AgCl reference electrode, which is expected to reduce the lithium content to around 50% compared to the previously studied over-lithiated samples. This assumption is based on ICP-OES measurements of similarly treated samples. Figure 4.5 displays the (111) reflection across the temperature range.



Figure 4.5: Displacement of the (111) peak of the LMO under nitrogen and oxygen atmosphere, across the temperature range from $25 \,^{\circ}$ C to $1200 \,^{\circ}$ C.

A significant shift of the peak towards lower angles with increasing temperature is again observed in the delithiated sample under an oxygen atmosphere. The first minimum in peak position appears at a significantly higher temperature, around 800 °C, followed by only a brief increase in the angle of the (111) reflex before the peak shifts again to a lower angles. At even higher temperatures, around 1100 °C, a second brief increase in angle occurs, after which the peak disappears completely at highest temperature at 1200 °C. This suggests that the thin film layer has undergone a transformation.

The lattice spacing was calculated from Bragg's law and plotted against temperature in Figure 4.6. The lattice expands as the temperature increases up to 800 °C, followed by a slight contraction. In contrast, the over-lithiated sample exhibits a noticeable reduction in lattice spacing at 500 °C. Although the exact mechanisms behind this behaviour are unclear, it is likely that oxygen is released at a later stage in the delithiated sample.

In a nitrogen atmosphere a similar behaviour is only observed up to $200 \,^{\circ}$ C. After that the lattice spacing increases much faster. Above $350 \,^{\circ}$ C the (111) reflection disappears completely, probably due to the amorphization of the thin film. The (222) reflection in this case is overlapped by a peak from the underlying platinum layer, making further analysis of this reflection impractical.



Figure 4.6: Variations of the lattice parameter of delithiated LMO under nitrogen and oxygen atmosphere determined from the (111) peak measured in the temperature range from $25 \,^{\circ}$ C to $1200 \,^{\circ}$ C.

4.2 SEM measurements

This section aims to provide an analysis of the surface behaviour of the LMO layer deposited on the YSZ crystal. To facilitate this investigation, two distinct samples were fabricated with LMO layer thicknesses of 80 nm (left) and 160 nm, respectively. A comparative evaluation of the surface morphology and characteristics of these layers was performed using scanning electron microscopy (SEM).

As shown in Figure 4.7, the SEM images of both samples, captured at a magnification of 80,000x, offer a detailed view of the surface features. This high magnification enables a closer examination of structural differences between the two thicknesses.



Figure 4.7: SEM images at $80,000 \times$ magnification of the LMO layers with thicknesses of 80 nm (left) and 160 nm (right), deposited on YSZ.

In both layer thicknesses, the characteristic pyramid-like structures of (400)-oriented spinel thin films of LMO are clearly visible. The size of these structures aligns well with depositions reported in the literature [27, 41], though the pyramids in this case appear in a more uniform and tightly packed pattern. This can be attributed to the fact that the LMO layer does not grow epitaxially in the (400) orientation across the entire surface. In the sample with the longer deposition time (left), larger surface structures are observed, accompanied by the formation of smaller grains on the surface.

Subsequent SEM imaging was performed on the samples previously analysed for the in situ XRD measurements. The corresponding images, presented in Figure 4.8, illustrate the surface morphology of the samples exposed to the two different atmospheres, O_2 (left) and N_2 (right). A magnification of 10,000x has been chosen for visualisation as the structures are significantly larger at this scale.



Figure 4.8: SEM images at $10,000 \times$ magnification of the LMO layers with 160 nm after the in situ XRD in O₂ (left) and N₂ (right) atmosphere, deposited on YSZ.

For both samples, a thermal treatment involving exposure to temperatures of up to 1200 °C, followed by rapid cooling, results in the formation of an amorphous surface. This thermal processing leads to the complete disappearance of the original pyramidal morphology observed in the layers prior to treatment.

Figure 4.9 displays the XRD patterns obtained at $50 \,^{\circ}$ C, illustrating the changes occurring before and after the temperature increase to $1200 \,^{\circ}$ C in an oxygen atmosphere. The analysis of these XRD patterns provides insights into the structural evolution of the material, demonstrating the deformation of the initial spinel structure.


Figure 4.9: Comparison of XRD measurements in an oxygen atmosphere at 50 °C, 1200 °C and 50 °C after reaching 1200 °C and rapid cooling.

The SEM image of the delithiated sample from subsection 4.1.3 under the oxygen atmosphere is shown in Figure 4.10.



Figure 4.10: SEM image at $10,000 \times$ magnification of a delithiated LMO layer with 80 nm after the in situ XRD in O₂ atmosphere, deposited on YSZ.

The structural change of the LMO thin film surface can also be seen here, although the structures are significantly smaller than in the previous case. Structurally different growth on the Pt grid is also clearly visible.

The SEM images provide valuable insights into the surface morphology of the LMO layers under varying conditions. A comparison of the different layer thicknesses and thermal treatments reveals notable differences in structural features, such as the size and distribution of surface grains. The high magnification images highlight the effects of temperature and atmospheric conditions on the thin film, including the change of the surface structure and variations in growth behaviour, particularly on the Pt grid.

4.3 Electrochemical impedance spectroscopy (EIS)

In the subsequent section, an in-depth analysis of the Electrochemical Impedance Spectroscopy (EIS) measurements is presented. The primary objective is to accurately identify and distinguish the various capacitances present within the system — ideally isolating a distinct chemical capacitance — alongside different types of resistances, including surface resistance, bulk resistance, and charge transfer resistance. These analyses aim to provide a more comprehensive understanding of the behaviour and dynamics of oxygen vacancies within the system.

The measurements are made in a three-dimensional parameter space defined by temperature T, oxygen partial pressure p_{O_2} and delithiation δ . While the addition of electrochemical variables would extend the analysis into a four-dimensional space, making it increasingly complex and potentially intractable, the approach adopted in this section is to isolate and consider the effects of each parameter individually. By separately examining the influences of temperature, oxygen partial pressure, and delithiation, it is possible to gain a clearer understanding of the specific contributions and interactions of each factor, thereby avoiding the complications that arise from the simultaneous variation of multiple parameters.

4.3.1 Models

Three models have been evaluated for the analysis of the impedance spectroscopy data and are discussed in more detail below. All models use a series resistor corresponding to the YSZ semicircle, which is also used for temperature control in the following segment.

YSZ feature

In the high-frequency region of the spectra (MHz), the characteristic feature of the YSZ single crystal can be observed, with resistance decreasing as temperature increases. Figure 4.11 illustrates the full impedance spectrum (left) and the high-frequency feature of the YSZ (right) at temperatures of 374 °C.

For further analysis the ionic conductivity of the YSZ single crystal is determined by the fitted bulk resistance R_{YSZ} , the surface area A_r , and the crystal thickness d:

$$\sigma_{\rm ion} = \frac{d}{R_{\rm YSZ} \cdot A_r} \tag{4.3}$$

Assuming approximately 0.1 mm was removed from all sides of the sample during polishing to prevent electrical short circuits, this results in an area reduction of about 10%. Thus the effective surface area of the YSZ crystal is reduced to:

$$A_r = 0.9 \cdot A_{\text{crystal}} \tag{4.4}$$



Figure 4.11: Full impedance spectrum (right) and the YSZ-feature (left), with T = 374 °C, $p_{O_2} = 200$ mbar and $\delta = 0.87$.

The temperatures from the measured value are calculated using an empirical equation based on a number of reference measurements. In Figure 4.12, the calculated and the via a thermocouple measured temperatures are compared for a slightly over-lithiated LMO ($\delta = 1.13$) layer at an oxygen partial pressure of 200 mbar.



Figure 4.12: Deviation between the calculated and measured temperatures as a function of ionic conductivity σ_{ion} at an oxygen partial pressure of $p_{O_2} = 200$ mbar and a delithiation of $\delta = 0.87$.

The deviations are therefore 0.4% of the absolute temperature at a measured temperature of 374 °C, increasing to approximately 1.1% at a measured temperature of 618 °C. The calculated temperatures are in good agreement with the theoretical model, particularly at lower temperature ranges where there is minimal deviation from the thermocouple readings. As the temperature increases, the YSZ resistance decreases, leading to greater discrepancies between

the experimentally measured and theoretically calculated temperatures. At maximum temperatures around 618 °C, the calculated temperature deviates significantly, reaching approximately 608 °C. This implies that the fitted YSZ resistance might be overestimated by about 15 %, corresponding to an offset of approximately 6 Ω between the calculated 41 Ω and the fitted 47 Ω . Part of this offset can be attributed to the resistance of the wiring and the contacts in the impedance spectroscopy setup, which ranges between 2 Ω and 3 Ω . This contribution becomes more significant at higher temperatures. Taking this additional resistance into account, the corrected YSZ resistance is 44 Ω , corresponding to a temperature of 613 °C.

As a verification, an ideal semicircle for the YSZ crystal at the lowest temperature of approximately 374 °C was fitted, with an additional offset resistance placed in series. This offset accounted for around 10% of the total resistance, bringing the calculated temperature closer to the measured value, with only a 0.2% deviation. At higher temperatures, it was no longer possible to fit this offset from the spectra. Thus, the calculated temperatures might be closer to the actual measurements than indicated in Figure 4.12, though this remains unverifiable.

For the further impedance spectroscopy analysis, the measured temperatures will be used, despite minor deviations from the actual sample temperatures as previously described. These differences between the fitted and calculated temperatures remain consistent across all spectra and will not be further discussed.

Model 1

The first model, as shown in Figure 4.13, consists of the YSZ resistance in series with a parallel R-CPE element. This R-CPE element serves as a simple model for determining the resistance and capacitance of the LMO thin film.



Figure 4.13: Model 1: YSZ resistance in series with an R-CPE element.

The model fits the experimental data best at lower temperatures, around $370 \,^{\circ}$ C. At this temperature, a nearly ideal semicircle with minimal suppression is typically observed (in addition to the YSZ feature), or at least the initial portion of the semicircle appears. More complex models would lead to overfitting in this case. As the temperature increases, the accuracy of this model diminishes, with the largest deviation occurring at 520 °C. At the highest temperature around 620 °C, the fits align more closely with the data once again. This model can be used

as an approximation for the magnitude of the chemical capacitance and serves as a basis for determining the desired capacitance in Model 2. A mechanistic interpretation of the resistance R_1 is speculative; it may represent the oxygen exchange resistance at the surface of the LMO layer.

Model 2

In Model 2, an additional R-CPE element is incorporated in series with the initial model to achieve a more accurate fit to the non-ideal nature of the semicircles. The configuration of Model 2 is illustrated in Figure 4.14.



Figure 4.14: Model 2: YSZ resistance in series with two R-CPE elements.

A significant challenge with this approach is the large uncertainties associated with the fit parameters. At lower temperatures, both R-CPE elements exhibit substantial inaccuracies in the estimation of capacitance and resistance, which can be attributed to over-parametrization. In contrast, the fits improve markedly at higher temperatures. Nevertheless, it remains challenging to unambiguously determine which of the two capacitances corresponds to the chemical capacitance of LMO. Moreover, it is even more difficult to attribute the two resistances to physical processes.

Model 3

In Model 3, a closed Warburg element is connected in parallel with a capacitor, as shown in Figure 4.15. The purpose of incorporating the Warburg element is to model the diffusion process occurring within the layer. However, despite this approach, the model sometimes displays significant deviations from the measured data, indicating limitations in accurately capturing all aspects of the electrochemical behaviour. The parallel capacitor is included to account for the electronic coupling at the YSZ/LMO interface in the ionic line of the transmission line model [27, 42].



Figure 4.15: Model 3: Transmission line model with no surface resistance.

Initially, additional resistances representing interfacial processes were integrated into the model. These resistances were intended to capture the effects associated with charge transfer at the LMO/YSZ and oxygen exchange at the surface. However, upon analysis, they were found to be negligibly small, with values ranging from the low ohm range down to levels that occasionally approached zero. Consequently, these resistances did not contribute to the models accuracy and were subsequently omitted from the final configuration.

Using this model, the bulk resistance of the ions, denoted as R_{ion} , can be directly extracted from the fitting procedure. Additionally, the chemical capacitance, C_{chem} , can be derived from the characteristic time constant of the Warburg element using the following relationship:

$$C_{chem} = \frac{\tau}{R_{bulk}} \tag{4.5}$$

This formulation provides a straightforward and unambiguous assignment of both the capacitance and resistance values, enhancing the clarity of the model. Nonetheless, the deviations from the experimental data remain more pronounced in this model compared to others. This discrepancy arises because the Warburg element in the current configuration integrates only infinitesimal ideal capacitors, rather than accounting for infinitesimal Constant Phase Elements (CPEs). As a result, the model's ability to accommodate non-idealities in the impedance response is limited, leading to a less accurate representation of the system's actual behaviour.

Model comparison

Next, a comparative analysis of the models will be conducted. To facilitate this comparison, Figure 4.16 displays three impedance spectra recorded at varying temperatures. All spectra were obtained under identical conditions of oxygen partial pressure ($p_{O_2} = 200 \text{ mbar}$) and a consistent degree of delithiation ($\delta = 0.87$). The spectra are analysed using the three different models discussed earlier. This comparative approach allows for a clearer assessment of how each model performs under the same experimental conditions, providing insight into their respective accuracies and suitability for describing the system's electrochemical behaviour at different temperatures.



Figure 4.16: Comparison of the three models and the measurement for the temperatures a) $374 \,^{\circ}$ C, b) $522 \,^{\circ}$ C and c) $618 \,^{\circ}$ C at an oxygen partial pressure of $p_{O_2} = 200$ mbar and a delithiation of $\delta = 0.87$.

In summary, the spectra exhibit an increasingly flattened low frequency semicircle as the temperature rises. At the lowest temperature, around $370 \,^{\circ}$ C, only a small portion of the semicircle is typically visible. However, performing fits at these lower temperatures is more challenging due to the limited number of data points available for fitting. This behaviour is observed across all samples, except for the highly over-lithiated sample with $\delta = 0.48$, and is consistent across all oxygen partial pressures. For the highly over-lithiated sample, even at temperatures around $370 \,^{\circ}$ C, a more complete semicircle is apparent, with overall resistances being smaller compared to other delithiation states.

Model 1 is able to adequately describe some of the experimental data. However, the majority of the spectra show larger deviations from this model, particularly around 500 °C, where Model 2 provides a significantly better fit. Model 3 can only be applied when a large portion of the semicircle is present, yet even in such cases, it exhibits pronounced deviations from the experimental data, as it fails to account for the non-idealities of the CPE. Despite these differences, the estimated capacitances remain within the same order of magnitude across all models.

4.3.2 Variation of the temperature

The first parameter to be investigated is the temperature dependence of capacitances and resistances across the different models. For the analysis of temperature dependence, sample D1, which exhibits a degree of delithiation of $\delta = 0.87$, has been selected for further investigation. The lithium content was prepared as after sputtering, without latter electrochemical lithium change. The δ value was obtained from ICP-OES analysis. In the following sections, the specific trends for this sample will be explored in depth, providing insight into the influence of temperature on capacitances and resistances as modelled by the three approaches discussed in this study.

Figure 4.17 illustrates the temperature dependence of the capacitances (left) and resistances (right) as determined by the three models for this sample. The sample is characterized by a slightly over-lithiated LMO layer, measured under an oxygen partial pressure of 200 mbar. The capacitances obtained from the fit were initially multiplied by a factor of 2 to represent a single electrode and subsequently normalized to the volume of the platinum-free interface of the thin film. The resistances were divided by 2 to correspond to a single electrode. It is important to note that C_{M3} reflects the chemical capacitance of the Warburg element rather than C_e .



Figure 4.17: Temperature dependence of the capacitances (left) and resistances (right) fitted from the three models at an oxygen partial pressure of $p_{O_2} = 200$ mbar and a delithiation of $\delta = 0.87$.

A clear relationship between capacitance and temperature is evident here, with capacitance

increasing as temperature rises across all models. In contrast, the resistances decrease with increasing temperature for all models. For the second capacitance, $C_{M2,2}$, in Model 2, this clear relationship is not consistently observed. In the mid to high temperature range, significant deviations in capacitance often occur, as seen in Figure 4.18 for a highly over-lithiated sample ($\delta = 0.48$), which underwent no electrochemical lithium modification following the sputtering process, at an oxygen partial pressure of 200 mbar.



Figure 4.18: Temperature dependence of the capacitances (left) and resistances (right) fitted from the three models at an oxygen partial pressure of $p_{O_2} = 200$ mbar and a delithiation of $\delta = 0.48$.

The capacitance $C_{M2,1}$ was determined using the R-CPE element that corresponds more closely to Model 1, and this is typically the R-CPE element with the larger resistance. As a result, $C_{M2,1}$ can be clearly identified in many spectra. The second R-CPE element, on the other hand, is mainly used to account for non-idealities. This additional semicircle often exhibits larger fit errors in both resistance and capacitance. In spectra measured at mid to high temperature ranges, the resistances of the two R-CPE elements tend to become occasionally similar, making it difficult to determine which of the two CPEs corresponds more accurately to the chemical capacitance.

The exponent n in the formula Equation 2.11 lies for the first model between 0.85 and 0.78 at low temperatures, and decreases with increasing temperature, reaching values between 0.7 and 0.6 at approximately 620 °C. This indicates that the non-ideality of the capacitor increases with temperature. This trend is also mostly valid for the first capacitance of the second model, with values in a similar range across the temperatures. The exponent n of the second CPE does not consistently follow this behaviour. The first capacitance in the second model and the capacitance in the first model typically fall within a similar range of values. The capacitance $C_{\rm M3}$ determined by Model 3 deviates more significantly at higher temperatures, reaching approximately double the capacitance at the maximum temperature of 620 °C.

Model 1 provides the best fit for the resistances at low temperatures. In contrast, Models 2 and 3 lack sufficient data at these temperatures to produce meaningful fits. It is only at higher temperatures that Model 2 begins to more accurately model the resistances. As shown in Figure 4.16, Model 3 tends to underestimate the resistances, and this behaviour is consistent across the entire temperature range. As the temperature increases, the resistance values across the models converge.

The precise determination of the chemical capacitance is not possible. However, its magnitude can be reasonably estimated within the range indicated by the different model calculations. Furthermore, the correlation between capacitance and temperature exhibits a comparable trend across all the models considered and a serve temperature dependence as also expected for such chemical capacitance.

Additional Arrhenius plots were created for the resistances and the capacitance derived from Figure 4.17 and Figure 4.18. In Figure 4.19, the Arrhenius plots for the resistance for samples D1 and D2, measured at an oxygen partial pressure of 200 mbar, are illustrated. The resistances were obtained using Model 1 and plotted against the reciprocal of the temperature.



Figure 4.19: The Arrhenius plots for the resistances determined using Model 1 of the sample D1 (left) and D2 (right) at an oxygen partial pressure of $p_{O_2} = 200$ mbar.

The activation energy (E_A) of the relevant resistance was calculated using the Arrhenius equation

for resistance, expressed as:

$$R = R_0 \cdot e^{-\frac{E_A}{k_B T}} \tag{4.6}$$

where R, R_0 , E_A , k_B , and T represent the resistance, the pre-exponential factor, the activation energy, the Boltzmann constant, and the temperature, respectively. The following expression is obtained by rearranging the Arrhenius equation:

$$\ln R = \ln R_0 + \frac{E_A}{k_B} \cdot \frac{1}{T} \tag{4.7}$$

From the slope k of the linear approximation, the activation energy in eV can be determined as follows:

$$E_A = \frac{k_B}{e} \cdot k \tag{4.8}$$

As illustrated in Figure 4.19, the activation energy is lower for sample D2, which has a higher lithium content. Both samples display a steeper gradient beginning around 470 °C, suggesting a change in the activation energy. This behaviour is similarly observed in the resistances calculated using Models 1 and 2. As mentioned above, a mechanistic interpretation of R_{M1} remains speculative, it may reflect the oxygen exchange at the surface.

The Arrhenius plots for the capacitance for samples D1 and D2, measured at an oxygen partial pressure of 200 mbar, are illustrated in Figure 4.20. The capacitances were obtained using Model 1 and plotted against the reciprocal of the temperature.



Figure 4.20: The Arrhenius plots for the capacitance determined using Model 1 of the sample D1 (left) and D2 (right) at an oxygen partial pressure of $p_{O_2} = 200$ mbar.

The activation energy of the capacitance for both samples is nearly identical. Compared to the Arrhenius plots of the resistance in Figure 4.19, both samples exhibit a steeper gradient that begins later, at approximately 520 °C.

The temperature dependence of parallel capacitor C_e in Model 3, is shown in Figure 4.21.



Figure 4.21: Temperature dependence of the capacitor C_e in Model 3 (Figure 4.15) at an oxygen partial pressure of $p_{O_2} = 200$ mbar and a delithiation of $\delta = 0.87$.

This capacitance only increases slightly with rising temperature, a trend that is consistently observed across all oxygen partial pressures and lithium contents of the samples. This behaviour is consistent with its proposed interpretation in Model 3, namely as an interfacial capacitance. The order of magnitude remains consistent across all other measurement series. At the lowest temperature of $370 \,^{\circ}$ C, C_{M3} is approximately five times larger than C_{e} , while at higher temperatures, the difference between these two values ranges from 1.5 to 2.5 orders of magnitude.

In general, as temperature increases, a consistent trend is observed: chemical capacitances substantially increase, and resistances strongly decrease across all the models under consideration. This behaviour aligns with expected thermodynamic and kinetic principles, where higher temperatures typically enhance ion mobility and reduce resistance to charge transport. Consequently, the observed increase in capacitance and reduction in resistance are coherent with the fundamental electrochemical behaviour.

The Model 2 deviates from this general trend more frequently than the other models. This discrepancy is attributed to the additional R-CPE element introduced in Model 2, which complicates the fit and introduces variability that is not as apparent in simpler models. The inclusion of the R-CPE component is designed to capture non-idealities in the impedance response, but it can also lead to inconsistencies, particularly in certain temperature ranges. This suggests that while Model 2 may offer a more nuanced approach, it may also be more sensitive to parameterization issues under varying temperature conditions.

This temperature dependent behaviour — increasing capacitance and decreasing resistance —

remains consistent across all delithiations and oxygen partial pressures. The consistency of this relationship across different experimental conditions provides further evidence of its importance in understanding how the material responds to thermal variations.

4.3.3 Variation of the oxygen partial pressure

The next variable to be examined is the oxygen partial pressure, which plays a significant role in influencing the electrochemical behaviour of the system. In the subsequent section, this dependence will be analysed in more detail to understand how variations in oxygen partial pressure affect the model parameters. For this analysis, the sample D1 will continue to be the focal point.

Sample D1 with $\delta = 0.87$

Figure 4.22 shows the variation of capacitance in the first model as a function of oxygen partial pressure for the sample under investigation. The plot presents the data across six different temperatures, providing insight into how the capacitance responds to changes in oxygen partial pressure at various thermal conditions.



Model 1: C_{M1} with $\delta = 0.87$

Figure 4.22: Oxygen partial pressure dependence of the capacitances determined using Model 1 for the different temperatures of sample D1 with a delithiation of $\delta = 0.87$.

A clear increase in capacitance with decreasing oxygen partial pressure is evident across all temperature ranges. The measurements began at a partial pressure of 1 mbar and was subsequently increased until the atmosphere reached 100 % oxygen content, i.e 1 bar O_2 . Following this, the two lowest partial pressures were measured. For the control measurements, indicated by dashed lines, the pressure was adjusted back to 1 mbar and 1 bar. Notably, a significant deviation was observed during the first measurement, likely because the sample had not yet fully equilibrated to the atmosphere at that point. This assumption is further supported by the control measurement at 1 mbar, conducted after the lowest partial pressure, which suggests incomplete equilibration. Theoretically, the possibility of a phase transformation at the beginning cannot be ruled out, but XRD measurements (Figure 4.23) before and after the experiments showed no changes in the diffraction patterns, suggesting no phase transformation occurred.



Figure 4.23: Comparison of XRD measurements before and after the EIS measurement for sample D1 with a delibilitient level of $\delta = 0.87$.

The second control point at an oxygen partial pressure of 1 bar shows that the capacitance decreases significantly, but the values remain higher compared to the initial measurements. Figure 4.22 clearly illustrates that at higher temperatures, the increase in capacitance becomes more pronounced as the oxygen partial pressure decreases. This increase in capacitance is further amplified at low oxygen partial pressures and high temperatures.

In the following Figure 4.24, the capacitances of the three models are displayed at different temperatures for the maximum $p_{O_2} = 1$ bar and the minimum $p_{O_2} = 0.2$ mbar. It is evident that the discrepancies between the models are smaller at higher temperatures and lower oxygen partial pressures compared to those at higher p_{O_2} values. Additionally, it can be observed that across nearly four orders of magnitude in partial pressure, the capacitance at a temperature of 618 °C increases by one order of magnitude, while for lower temperatures, this gradient is less pronounced.



Figure 4.24: Temperature dependence of the capacitances fitted from the three models at an oxygen partial pressure of $p_{O_2} = 1$ bar (left) and $p_{O_2} = 0.2$ mbar (right) with $\delta = 0.87$.

In Figure 4.25, the three models are compared across the full range of oxygen partial pressures for temperatures of 618 °C and 374 °C. This comparison provides insight into how each model behaves under varying oxygen partial pressures at both high and low temperature extremes.

 C_{Mi} with $\delta = 0.87$ 4.0 3.0 618 °C log(C_{Mi}) [F/cm³] 2.0 374 °C 1.0 -Model 1 Measuring -Model 2 Model 3 0.0 0.0 1.0 3.0 -1.0 2.0 log(po2) [mbar]

Figure 4.25: Oxygen partial pressure dependence of the capacitances determined using the three models for the temperatures of 618 °C and 374 °C of the sample D1 with $\delta = 0.87$.

At higher oxygen partial pressures, Model 1 demonstrates a lower capacitance in comparison to Model 2. As the oxygen partial pressure decreases, the discrepancy between the two models narrows. At a pressure of 0.5 mbar, the relationship reverses, with Model 1 recording a higher capacitance. This indicates that Model 2 demonstrates a comparatively lower increase in capacitance with decreasing oxygen partial pressure in comparison to Model 1. The behaviour of the slopes $k(p_{O_2}, C_i)$ is clearly visible for all temperatures in Figure 4.26.



Figure 4.26: Gradient of capacitances across the full range of oxygen partial pressure for the three models, shown as a function of temperature for the delithiation level $\delta = 0.87$.

A study examined the behaviour of oxygen release from LMO at temperatures between 600 °C and 850 °C under varying oxygen partial pressures. At an oxygen partial pressure of 0.2 mbar and a temperature of 600 °C, a δ_{O_2} value of approximately 0.06 was observed. At higher temperatures, a phase transition, as discussed in section subsection 4.1.2 is also confirmed here, with a significantly increased oxygen release, reaching a δ_{O_2} value of up to 0.67 [43]. This suggests that the measured capacitance indeed reflects the variation of the oxygen content either by the presence of oxygen vacancies or cation interstitials.

In comparison to the other models, Model 3 demonstrates a notably higher capacitance across all oxygen partial pressures, with the most significant discrepancy occurring at higher pressures. As the oxygen partial pressure decreases, the capacitance of Model 3 approaches the values of the other two models. The rate of capacitance increase in Model 3 is comparable to that observed in Model 2.

As shown in Figure 4.26, a continuous increase in the gradient of the capacitances with rising temperatures is observed in all three models. The gradients of the logarithmic values of capacitance and oxygen partial pressure start at approximately -0.05 for Models 2 and 3 at a temperature of 374 °C, gradually increasing to just below -0.20 at 618 °C. In Model 1, the gradient varies between -0.09 and -0.24 at the highest temperature.

In Figure 4.27, the resistance obtained from the first model is plotted against the oxygen partial pressure for various temperatures, illustrating this behaviour.



Model 1: R_{M1} with $\delta = 0.87$

Figure 4.27: Oxygen partial pressure dependence of the resistances determined using Model 1 for the different temperatures of sample D1 with a delithiation of $\delta = 0.87$.

There is no clear dependence observed in the determined resistances across the different oxygen partial pressures. For the majority of oxygen partial pressures, the resistance determined by the first model remains nearly constant. The initial measurement, conducted at an oxygen partial pressure of 1 mbar, likely accounts for the lower resistance value, as the sample had probably not yet fully equilibrated with the atmosphere, as previously noted in the capacitance measurements. At the lowest partial pressures of 0.2 mbar and 0.5 mbar, a distinct increase in resistance is observed, with this effect becoming more pronounced at higher temperatures. The resistance reverts to approximately its initial value after the oxygen partial pressure is raised to $p_{O_2} = 1$ bar during the control measurements.

In the following Figure 4.28, the resistances determined by the three different models are plotted against the oxygen partial pressure for the temperatures of 374 °C and 618 °C.



Figure 4.28: Oxygen partial pressure dependence of the resistances determined using the three models for the temperatures of 618 °C and 374 °C of the sample D1 with $\delta = 0.87$.

In summary, the reduction in oxygen partial pressure results in a consistent increase in capacitance across all models. This trend is clearly observable in most cases, with only a few outliers deviating from the general behaviour. The relationship between oxygen partial pressure and capacitance is well-defined, demonstrating a direct correlation across the full range of examined partial pressures and temperatures.

A similarly distinct relationship between oxygen partial pressure and resistance is not as apparent. For the majority of temperature ranges, the resistances exhibit minimal variation and remain nearly constant across different partial pressures. Unlike the capacitances, the resistances do not show a clear, systematic dependence on the reduction of oxygen partial pressure.

At higher temperatures, however, more significant deviations in resistance are observed. In particular, at lower oxygen partial pressures, resistances tend to increase. These elevated resistances at low partial pressures are especially noticeable at elevated temperatures, where the system's behaviour deviates more prominently from the trend seen at lower temperatures. This suggests that, while capacitance exhibits a well-defined dependency on oxygen partial pressure, the relationship between resistance and oxygen partial pressure is less predictable and not as clearly defined.

4.3.4 Variation of the lithium content

The final parameter examined is the lithium content. This section focuses on how the lithium content of the various samples influences the electrochemical properties in each of the models. For this analysis, five samples with varying levels of delithiation were selected, each representing a different lithium content. These samples are summarized in Table 4.1, where their specific lithium contents are listed. The aim of this investigation is to assess the extent to which these variations in lithium concentration affect parameters such as capacitance, resistance, and overall electrochemical response.

Table 4.1: Lithium content of the examined samples measured by ICP-OES and the corresponding voltage used for the delithiation process.

Sample	x in $Li_xMin_2O_4$	Delithiation voltage
D1	1.13	no delithiation
D2	1.52	no delithiation
D3	0.73	$0.9\mathrm{V}$
D4	0.66	$1.0\mathrm{V}$
D5	0.32	1.1 V
D3 D4 D5	0.73 0.66 0.32	0.9 V 1.0 V 1.1 V

т• ъл

Until now, the primary focus has been on the slightly over-lithiated sample D1, which exhibits a delithiation degree of $\delta = 0.87$. The precise lithium content for this and other samples was determined using ICP-OES measurements. Both samples D1 and D2 were not subjected to delithiation processes, with D2 showing a notably higher lithium content compared to the sample D1. Interestingly, while the LMO target itself is slightly over-lithiated, control measurements indicate that its lithium content is closer to that of D1.

The significant discrepancy in lithium content between D2 and D1 is intriguing, especially considering that the sputtering process parameters such as pressure, power and deposition time were identical for both samples. This inconsistency in lithium content is not readily explainable within the context of the experimental conditions, and further investigation may be required to understand the cause of this variance, including further validation tests of the ICP-OES measurements.

The other three samples, underwent delithiation according to the procedure outlined in the section subsection 3.1.4, where the delithiation process was carried out in a cell containing aqueous electrolytes. These delithiated samples provide a broader perspective on how varying lithium concentrations impact the electrochemical properties under investigation.

Sample D2 with $\delta = 0.48$

The capacitances of this significantly over-lithiated sample, corresponding to six different temperatures, are illustrated in Figure 4.29 as a function of the oxygen partial pressure.





Figure 4.29: Oxygen partial pressure dependence of the capacitances determined using Model 1 for the different temperatures of sample D2 with a delithiation of $\delta = 0.48$.

For this sample, measurements were conducted starting from a fully oxygenated atmosphere, gradually decreasing to the lowest partial pressure of 0.2 mbar. To verify the results, supplementary measurements were performed at oxygen partial pressures of 0.5 mbar and 1 bar. The temperature behaviour of this sample is similar to that of the previously examined sample D1, with capacitance increasing for each partial pressure as the temperature rises. However, across almost the entire range of measurements, the capacitance of this sample is approximately half an order of magnitude lower than that of the previously analysed sample with $\delta = 0.87$. Only at high partial pressures and elevated temperatures does the capacitance approach levels comparable to those of sample D1. Additionally, the capacitances in this sample are much more

stable across the range of partial pressures.

Between temperatures of 366 °C and 515 °C, a slight increase in capacitance is observed, reaching a maximum at $p_{O_2} = 10$ mbar, followed by a decrease at lower partial pressures. Only at the lowest oxygen partial pressure of 0.2 mbar is there a notable increase in capacitance over the entire temperature range. At the highest temperature, a more pronounced dependence on partial pressure is observed across the entire range. The control measurements taken after reaching the lowest oxygen partial pressure show significant deviations. At $p_{O_2} = 0.5$ mbar, the capacitance decreases for temperatures between 515 °C and 612 °C, but doesn't return to the values recorded in the initial measurements at this point. Interestingly, at lower temperatures, the capacitance increases compared to that at $p_{O_2} = 0.2$ mbar. A possible explanation for this behaviour is the release of lithium. The thermal stress under low partial pressures could induce delithiation in this highly over-lithiated sample.

In Figure 4.30, the capacitances determined using the second model are illustrated.



Model 2: $C_{M2,1}$ with $\delta = 0.48$

Figure 4.30: Oxygen partial pressure dependence of the capacitances determined using Model 2 for the different temperatures of sample D2 with a delithiation of $\delta = 0.48$.

For this sample, the behaviour at high temperatures in the second model is similar to that of Model 1. At lower temperatures, there are greater fluctuations and deviations from the nearly constant capacitances observed in Model 1. Notably, large variations in the second capacitance frequently occur, as can also be seen in Figure 4.25. The resistances in this model also exhibit greater variability, often making it unclear which of the two R-CPE elements provides a better description of the systems behaviour. This is particularly evident at approximately 515 °C in the low partial pressure range. Compared to Model 1, significantly higher capacitances are achieved in the second model at low partial pressures and temperatures between 416 °C and 515 °C. To further examine the differing behaviour of the models, Figure 4.31 illustrates the fitted capacitances of the models for sample D2 at an oxygen partial pressure of $p_{O_2} = 1$ mbar.



Figure 4.31: Temperature dependence of the capacitances (left) and resistances (right) fitted from the three models at an oxygen partial pressure of $p_{O_2} = 1$ mbar with $\delta = 0.48$.

It is important to note that at temperatures between $416 \,^{\circ}\text{C}$ and $515 \,^{\circ}\text{C}$, the capacitance is often not clearly defined. For the analysis in Figure 4.30, the capacitance associated with the resistance that most closely aligns with Model 1 was consistently selected. In many cases, the second resistance is noticeably smaller than that of Model 1. However, at lower partial pressures, the resistances are of a similar magnitude, making it challenging to determine the capacitances accurately.

The capacitance behaviour in Model 3, as depicted in Figure 4.32, largely mirrors that observed in Model 1. Similar to the findings for sample D1 in Figure 4.22, the capacitances in Model 3 are significantly higher compared to those in Models 1 and 2. Across nearly the entire range, the capacitances in Model 3 are approximately twice the values of those observed in Model 1. At a temperature of 515 °C, a pronounced increase in capacitance is observed at the lowest partial pressure of 0.2 mbar.



Model 3: C_{M3} with $\delta = 0.48$

Figure 4.32: Oxygen partial pressure dependence of the capacitances determined using Model 3 for the different temperatures of sample D2 with a delithiation of $\delta = 0.48$.

The comparison of the gradients in Figure 4.33 further highlights the differences between the models, making the deviations more apparent.



Figure 4.33: Gradient of capacitances across the full range of oxygen partial pressure for the three models, shown as a function of temperature for the delibilition level $\delta = 0.48$.

The fluctuations in Model 2 are particularly noticeable when compared to the other models. In contrast to Figure 4.26, the gradients for this sample with a delithiation level of $\delta = 0.48$ are lower for both Models 1 and 3. The differences in gradients between the two models are smaller at most temperatures than those observed in the previously examined sample with $\delta = 0.87$. However, the absolute capacitance values remain significantly higher in Model 3, approximately double those of Model 1.

The behaviour of the resistances for sample D2, as modelled by Model 1, is shown in Figure 4.34 as a function of oxygen partial pressure.



Figure 4.34: Oxygen partial pressure dependence of the resistances determined using Model 1 for the different temperatures of sample D2 with a delithiation of $\delta = 0.48$.

The measurements were taken from the highest to the lowest partial pressure, and then increased again to 1 bar after the point at 0.5 mbar. In general, the resistances are lower and exhibit greater variation compared to the sample with $\delta = 0.87$. For the highest temperature, the resistance increases as the partial pressure decreases. However, for progressively lower temperatures, this behaviour reverses, except at the lowest oxygen partial pressure. At a pressure of 0.2 mbar, the resistance increases across all temperatures, with this effect being more pronounced at lower temperatures. When the partial pressure is increased again, the resistances remain significantly elevated compared to the values measured at the same points earlier. This holds true for all temperatures examined.

In Figure 4.35, the resistances of the three models are illustrated for temperatures of 366 °C and 612 °C. The resistances in Models 2 and 3 show minimal divergence from those in Model 1. Model 2 exhibits greater fluctuations only at the lowest temperature and at low partial pressures. In Model 3, the resistances are generally lower than in the other models, although this difference is less pronounced than it was for sample D1.



Figure 4.35: Oxygen partial pressure dependence of the resistances determined using the three models for the temperatures of 612 °C and 366 °C of the sample D2 with $\delta = 0.48$.

Sample 03 with $\delta = 1.27$

The first delithiated sample was discharged to a voltage of 0.9 V against the Ag/AgCl reference electrode. This process was intended to remove approximately half of the lithium from the cathode. Figure 4.36 illustrates one cycle of sample D3 and the discharge process down to a voltage of 0.9 V.



Figure 4.36: Comparison of a cycle of the sample D3 ($\delta = 1.27$) in aqueous electrolyte with the discharge curve down to 0.9 V.

The samples, based on their geometry, were theoretically expected to circulate a charge of 8.75 mC, corresponding to the transition from LiMn_2O_4 to the fully delithiated state of Mn_2O_4 . According to the discharge curve, 5.3 mC were removed during this cycle, indicating that the sample may not have been fully contacted by the platinum wire as described in subsection 3.1.4. The charge extracted up to the 0.9 V threshold corresponds to 3.9 mC.

It is important to note that side reactions in the aqueous electrolyte, caused by electrolysis at these voltages, can shift the current-voltage characteristics, making it difficult to accurately determine the state of charge from the curve. Additionally, since the samples were over-lithiated during the sputtering process, as previously described, it is generally challenging to make precise statements about the cathode's state of charge. For this reason, the samples were analysed for their exact stoichiometry using ICP-OES measurements following the EIS experiments to better define the state of charge. In this case, the stoichiometry was determined to be $Li_{0.73}Mn_2O_4$.

The same conditions apply to the further delithiated samples, D4 and D5, with the exception that they were discharged to 1 V and 1.1 V, respectively.

In Figure 4.37, the capacitances of the first model for the sample with $\delta = 1.27$ are shown. The measurements were conducted by gradually reducing the oxygen partial pressure from 1 bar to 0.2 mbar, followed by a successive increase back to 1 bar.



Model 1: C_{M1} with $\delta = 1.27$

Figure 4.37: Oxygen partial pressure dependence of the capacitances determined using Model 1 for the different temperatures of sample D3 with a delithiation of $\delta = 1.27$.

The behaviour of the capacitance as a function of both temperature and oxygen partial pressure follows a pattern similar to that observed in the over-lithiated samples. As temperature increases and the oxygen content in the atmosphere decreases, a corresponding increase in capacitance is consistently observed. In contrast to the previously examined over-lithiated samples, the capacitance values at higher to mid-level partial pressures, ranging from 1 bar to approximately 5 mbar, are significantly lower. This suggests that the degree of lithiation has a notable influence on the overall electrochemical response, particularly at these partial pressures.

At the lowest temperature, the capacitance remains comparable to the sample with $\delta = 0.87$, indicating similar behaviour under cooler conditions. As the temperature increases, the differences between the capacitances of the two samples become increasingly pronounced.

Starting at an oxygen partial pressure between 5 mbar and 10 mbar, the capacitance of this sample begins to exhibit an earlier and steeper increase in gradient compared to the over-lithiated samples. This leads to a scenario where, at lower partial pressures, this sample surpasses the capacitance observed in the over-lithiated case.



 C_{Mi} with $\delta = 1.27$



Figure 4.38: Oxygen partial pressure dependence of the capacitances determined using the three models for the temperatures of 618 °C and 374 °C of the sample D3 with $\delta = 1.27$.

The second model shows more pronounced fluctuations, similar to those observed in samples D1 and D2. In this case, the capacitances and resistances of the two R-CPE elements frequently fall within the same order of magnitude, accompanied by increased errors in the second model. As shown in Figure 4.38, the third model exhibits deviations in behaviour only around 370 °C. This is attributed to the insufficient visibility of the non-ideal semicircle in the spectra, preventing a reliable fit of the data using this model. The earlier, more rapid increase in capacitance is also evident in this model. Once again, the capacitances in Model 3 are significantly higher than those in Models 1 and 2. The fitted capacitances at lower oxygen partial pressures are elevated for the lower temperatures compared to Model 1, while at the two highest temperatures, they have a similar value. At the highest temperature, the capacitance in the third model approaches that of the first model as the oxygen partial pressure decreases.

In Figure 4.39, the gradients of the capacitances across the three models are illustrated over the entire range of oxygen partial pressures for all temperatures. In case of the sample D3, a significantly steeper gradients are observed depending on the model, ranging from -0.3 to -0.4 at the two highest temperatures. In contrast to the sample D2 ($\delta = 0.48$) which only exhibited gradients up to -0.15, while sample D1 ($\delta = 0.87$) reached a maximum gradient of -0.25.



Figure 4.39: Gradient of capacitances across the full range of oxygen partial pressure for the three models, shown as a function of temperature for the delithiation level $\delta = 1.27$.



Figure 4.40: Oxygen partial pressure dependence of the resistances determined using Model 1 for the different temperatures of sample D3 with a delithiation of $\delta = 1.27$.

The resistances determined using the first model, as shown in Figure 4.40, increase steadily at the highest temperatures. At lower temperatures, a saturation behaviour in the resistances appears to occur in the range of lower partial pressures. This resistance behaviour is similar in Model 2. For Model 3, a smaller gradient is observed at the lowest temperature in the low partial pressure range, while for all other temperatures, a similar saturation behaviour in the resistances is evident. As previously noted, the resistances in Model 3 are consistently fitted to lower values compared to the other two models. The resistance behaviour of this sample differs from the previously examined over-lithiated samples. The order of magnitude is similar to the sample D1 with $\delta = 0.87$.

Sample D4 with $\delta = 1.34$

The next sample subjected to further delithiation, is analysed. The delithiation process was carried out until a voltage of 1.0 V was reached against the Ag/AgCl reference electrode. According to the ICP-OES measurements, this procedure adjusted the sample to the stoichiometric composition of $Li_{0.66}Mn_2O_4$. The capacitance determined by Model 1 for the sample with $\delta = 1.34$ is shown in Figure 4.41





Figure 4.41: Oxygen partial pressure dependence of the capacitances determined using Model 1 for the different temperatures of sample D4 with a delithiation of $\delta = 1.34$.

The behaviour of the capacitances is very similar to that of sample D3 ($\delta = 1.27$). Except the point at the highest temperature and that at lowest partial pressures, the capacitance has decreased in comparison do the previous sample. The increase in capacitance is more continuous over changes in partial pressure. Only at the two highest temperatures a significant increase in the gradient at low oxygen partial pressures is noticeable. Model 2 exhibits the same issues as observed with the previous sample.

The capacitance determined using the third model is presented in Figure 4.42. In this case, there is an even more continuous increase in capacitance as the oxygen partial pressure decreases. Additionally, the graphs for the individual temperatures are more evenly distributed across the capacitance range compared to the first model. In the region of high partial pressures, the capacitances are significantly higher than those of the first model. For the highest temperature and the lowest oxygen partial pressure, a lower capacitance is obtained using Model 3.



Model 3: C_{M3} with $\delta = 1.34$

Figure 4.42: Oxygen partial pressure dependence of the capacitances determined using Model 3 for the different temperatures of sample D4 with a delithiation of $\delta = 1.34$

The gradients of capacitance versus oxygen partial pressure for the three models at different temperatures are shown in Figure 4.43. It is important to note the aforementioned increased uncertainties associated with Model 2. Initially, the gradients of Models 1 and 3 are similar, but starting from temperatures around 519 °C, a more pronounced divergence occurs. Compared

to the sample with $\delta = 1.27$, the gradients are slightly lower. For the highest temperature, the gradients across the models range from -0.22 to -0.34.



Figure 4.43: Gradient of capacitances across the full range of oxygen partial pressure for the three models, shown as a function of temperature for the delithiation level $\delta = 1.34$.

In Figure 4.44, the resistances of sample D4 ($\delta = 1.34$) are shown as a function of oxygen partial pressure at different temperatures.



Figure 4.44: Oxygen partial pressure dependence of the resistances determined using Model 1 for the different temperatures of sample D4 with a delithiation of $\delta = 1.34$.

The behaviour of the resistances is very similar to that of the previously examined sample with $\delta = 1.27$, although the resistances are generally slightly higher. At lower temperatures, the resistances remain constant across a wide range of partial pressures. However, at the two highest temperatures, the dependence of resistance becomes more pronounced compared to sample D3. This dependency can also be recognised in Model 2, although considerable fluctuations are observed due to the larger errors caused by the use of the two R-CPE elements.

The resistances fitted with Model 3 are shown in Figure 4.45. As with the previously analysed samples, the resistances remain much more stable across different partial pressures and, similar to previous observations, the resistances determined using Model 3 are significantly smaller than those calculated using Models 1 and 2.



Model 3: R_{M3} with $\delta = 1.34$

Figure 4.45: Oxygen partial pressure dependence of the resistances determined using Model 3 for the different temperatures of sample D4 with a delithiation of $\delta = 1.34$.

The sample D4 ($\delta = 1.34$), underwent further delithiation and exhibited behaviours similar to previous samples, particularly sample D3 ($\delta = 1.27$). The capacitance increased steadily with decreasing oxygen partial pressure, with notable differences emerging at higher temperatures. Model 2 continued to show greater uncertainties due to the use of two R-CPE elements, resulting in fluctuations. In contrast, Model 3 provided more consistent and stable results across partial pressures, with its resistances significantly lower than those of Models 1 and 2. Overall, the trends in capacitance and resistance behaviour were in line with previously observed patterns.

Sample D5 with $\delta = 1.68$

A sample delithiated at a voltage of 1.1 V against the Ag/AgCl reference electrode is finally analysed. According to the ICP-OES measurements, sample D5 has a stoichiometric composition of Li_{0.32}Mn₂O₄. The capacitance determined with the first model is shown in Figure 4.46 as a function of oxygen partial pressure at different temperatures. Similar to previous tests, the oxygen content was gradually reduced from 100% atmospheric conditions and then increased.



Model 1: C_{M1} with $\delta = 1.68$

Figure 4.46: Oxygen partial pressure dependence of the capacitances determined using Model 1 for the different temperatures of sample D5 with a delithiation of $\delta = 1.68$.

Figure 4.47 presents a comparison of the gradients of the capacitances over the oxygen partial pressure for sample D5 across all temperatures and models. The behaviour of the gradients in the first model closely resembles that of sample D4 ($\delta = 1.34$). In Model 3, significant deviations are only observed at the temperature of 474 °C. In contrast, Model 2 again exhibits increased



fluctuations, particularly in the high-temperature range.

Figure 4.47: Gradient of capacitances across the full range of oxygen partial pressure for the three models, shown as a function of temperature for the delithiation level $\delta = 1.68$.

The resistances of the first model, as depicted in Figure 4.48, also display behaviour very similar to that of the sample with $\delta = 1.34$. This similarity extends to the other two models as well.



Figure 4.48: Oxygen partial pressure dependence of the resistances determined using Model 1 for the different temperatures of sample D5 with a delithiation of $\delta = 1.68$.

Even with this significant degree of delithiation $\delta = 1.68$, the behaviour remains very similar to that of the previously analysed samples with higher lithium content. The capacitances are slightly lower than those in the previously analysed delithiated samples D3 and D4.

Comparison of the different degrees of delithiation

For a more detailed comparison of the behaviour of samples with varying lithium content, Figure 4.49 illustrates the relationship between capacitance and oxygen partial pressure at temperatures of 370 °C and 620 °C, with capacitance values derived from the first model.



Model 1: C_{M1} for various δ

Figure 4.49: Oxygen partial pressure dependence of the capacitances determined using Model 1 for the temperatures of 618 °C and 373 °C with various delithiations.

At lower temperatures around 373 °C, there is little to no increase in capacitance across the samples. The sample with the highest lithium content exhibits the lowest capacitance values. At higher temperatures around 616 °C, a clear increase in capacitance is observed across all delithiated samples. These samples display very similar behaviour across the oxygen partial pressure range at elevated temperatures, starting from nearly the same value of approximately 80 F/cm^3 at $p_{\text{O}_2} = 1$ bar and reaching a maximum within the same range, between 2730 F/cm^3 and 3760 F/cm^3 at $p_{\text{O}_2} = 0.2 \text{ mbar}$. The sample with $\delta = 0.87$ also reaches this range, but it
starts from a considerably higher value of around $150 \,\mathrm{F/cm^3}$. In contrast, the sample with the highest lithium content ($\delta = 0.48$) only reaches a significantly lower capacitance of $850 \,\mathrm{F/cm^3}$ at $p_{\mathrm{O}_2} = 0.2 \,\mathrm{mbar}$. Over a broad range, this sample (D2) exhibits a higher capacitance than the delithiated samples.

To provide clearer visualization, the slopes of the capacitances for the different degrees of delithiation over temperature, as determined by the first model, are shown in Figure 4.50.



Figure 4.50: Gradient of capacitances across the full range of oxygen partial pressure for the various deliberation levels, shown as a function of temperature.

All samples exhibit an increase in the gradient of capacitance with rising temperatures. The most over-lithiated sample consistently displays the lowest gradient across all temperatures. The sample with $\delta = 0.87$ shows a higher gradient at lower temperatures, but the delithiated samples reach higher gradients at the two highest temperatures. The sample with $\delta = 1.27$ demonstrates a notably higher gradient in the mid-temperature range compared to the other delithiated samples. However, this sample also achieves a similar capacitance gradient at 620 °C, reaching -0.36, while the other two samples exhibit values around -0.34.

Figure 4.51 presents the resistances, fitted using the first model, as a function of oxygen partial pressure at temperatures of 370 °C and 620 °C for the samples under consideration. The resistance of the sample with $\delta = 0.48$ at a temperature of 370 °C shows the most significant deviation from the other delithiated samples. Across the majority of the measurements, its resistance is 1 to 2 orders of magnitude lower than that of the other samples. A clear trend in resistances at low temperatures is not evident here. It is important to note that, aside from the sample with $\delta = 0.48$, only a small portion of the semicircle was available for fitting at low temperatures, potentially leading to inaccuracies. However, these inaccuracies are not substantial enough to diminish the observed difference in resistance between sample D2 and the other samples.



Model 1: R_{M1} for various δ

Figure 4.51: Oxygen partial pressure dependence of the resistances determined using Model 1 for the temperatures of $618 \,^{\circ}$ C and $373 \,^{\circ}$ C with various delibilitations.

At higher temperatures, the samples exhibit more similar behaviour, with resistances increasing as the oxygen partial pressure decreases. For the sample with $\delta = 0.87$, this trend is only apparent at the lowest range of oxygen partial pressure, while across the remaining range, the resistance remains relatively constant.

The study analysed several samples with varying degrees of delithiation to examine their electrochemical properties, focusing on capacitance and resistance across different temperatures and oxygen partial pressures. The most over-lithiated sample ($\delta = 0.48$) showed the lowest capacitances, reaching a maximum of 850 F/cm³ at low oxygen partial pressures of 0.2 mbar, while its resistances were 1 to 2 orders of magnitude lower than the others at low temperatures. In contrast, all the samples with a lower lithium content like D3 ($\delta = 0.87$) exhibited significantly higher capacitances, particularly at elevated temperatures, where they achieved a maximum of 2730–3760 F/cm³. In addition, all samples showed an increased capacitance gradient at lower oxygen partial pressures.

At higher temperatures, resistances increased with decreasing oxygen partial pressure for all

samples, though the sample with $\delta = 0.87$ maintained relatively constant resistance over most of the partial pressure range. The delithiated samples, especially D4 and D5, showed very similar trends in capacitance and resistance, with resistances higher than those of the overlithiated sample.

Overall, an unexpectedly stable behaviour was observed across all delithiation levels, suggesting that no significant phase transformation of LMO occurred during the experiments, despite the relative strong changes in defect concentrations that can be assumed as cause of the observed changes in chemical capacitance. The capacitance and resistance behaviours were primarily influenced by temperature and oxygen partial pressure, with the delithiated samples exhibiting more pronounced changes.

As mentioned previously, a detailed mechanistic interpretation of the obtained resistances and capacitances is beyond the scope of this thesis. However, a few preliminary conclusions can still be drawn:

The absolute capacitance values of approximately 100 F/cm^3 or even more at low oxygen partial pressure and elevated temperatures, can only be attributed to chemical storage processes, as they far exceed typical interfacial capacitance values per area $(1 \text{ mF/m}^2 \text{ range for high } p_{O_2} \text{ values versus approximately } 100 \text{ }\mu\text{F/}\mu\text{m}^2)$. Chemical capacitances are determined by the minority charge carrier concentration c_{\min} via [44]:

$$C_{\rm chem} = \frac{e^2}{k_B T} \cdot Z_{\rm min}^2 \cdot c_{\rm min} \tag{4.9}$$

where $Z_{\rm min}$ represents the charge number of the minority defect. The observed dependence of the capacitance on p_{O_2} suggests an ionic minority defect, potentially oxygen vacancies or cation interstitials. Assuming oxygen vacancies ($Z_{\rm min} = 2$), the vacancy concentration can be estimated to be approximately $1.2 \cdot 10^{19} \,\mathrm{cm}^{-3}$ based on $C_{\rm chem} = 100 \,\mathrm{F/cm}^3$ at around 620 °C. At the lowest oxygen partial pressures, maximal values of about $3200 \,\mathrm{F/cm}^3$ correspond to a vacancy concentration of $3.8 \cdot 10^{20} \,\mathrm{cm}^{-3}$, which is in the 10^{-2} range with respect to oxygen lattice sites. This is certainly a conceivable value.

Regarding resistance, the effects of p_{O_2} on transport limitations and oxygen exchange as ratelimiting steps can be compared. At lower p_{O_2} , an increase in oxygen vacancies (or cation interstitials) would be expected, resulting in a decrease in transport resistance. However, this contrasts with some observed results. For oxygen exchange, a balance between defect concentration (increasing with decreasing p_{O_2}) and the availability of gas molecules (decreasing at lower p_{O_2}) may lead to a moderate or low dependence on p_{O_2} . This provides initial insights of what may happen in spinel oxides when using them in the oxygen world.

4.4 Circulation capability

The final step is to determine whether the samples can still be cycled after EIS measurements at low oxygen partial pressures and a temperature up to 618 °C, and how their cycling behaviour compares to that prior to EIS measurements. This analysis was performed by cycling the sample in a cell containing aqueous electrolytes as described in subsection 3.1.4. Between cycles, EIS measurements were performed at oxygen partial pressures of 10 mbar, 1 mbar, and 0.2 mbar, with temperature cycling performed in each case. Figure 4.52 shows the capacitances and resistances determined from the EIS measurement models at an oxygen partial pressure of 1 mbar over different temperatures.



Figure 4.52: Temperature dependence of the capacitances(left) and resistances (right) at an oxygen partial pressure of $p_{O_2} = 1$ mbar.

The magnitude and behaviour of the two variables are comparable to those of the samples analysed in the previous section. However, the second capacitance determined by the second model shows greater deviations at lower temperatures, likely due to over-parametrization of the impedance model in this range.

Figure 4.53 provides a comparison of four cycles, two before and two after the EIS measurement. Cycling of the sample remains possible following the EIS measurement. During the first cycle before the EIS measurement — which is also the very first measured cycle — an increased lithium extraction at low voltages is observed, suggesting an initial over-lithiation of the as-prepared sample. This behaviour does not recur in subsequent cycles. In the second cycle before impedance spectroscopy, significantly less lithium is extracted, while the lithium insertion is slightly elevated.



Figure 4.53: Comparison of the current-voltage characteristics for the first two cycles of the LMO thin film in aqueous electrolyte before and after the EIS measurements at temperatures up to $T = 618^{\circ}$ C and $p_{O_2} = 0.2$ mbar.

After the EIS measurements, the subsequent cycle exhibits a notably higher current than the second measurement, indicating a greater amount of lithium insertion. The current reaches the same values as in the first cycle. Lithium extraction is also elevated compared to the measurements prior to the EIS measurement. The second cycle after the EIS measurement reveals a lower lithium extraction than that of the first post-EIS cycle, with the extraction level aligning closely with that of the first post-EIS measurement. Additionally, the current peaks of the cycles shift to higher voltages following the EIS measurements. The position of the peaks, particularly in lithium insertion, remains unchanged between the two post-EIS cycles, suggesting the possibility of a partial phase transformation.

A thorough analysis is hindered due to the issues described in section 4.3.4 related to the setup of the cell with aqueous electrolytes. To achieve a more precise cycling experiment, it would be necessary to utilize organic electrolytes and fully contacted samples in order to conduct well-defined cycling.

Chapter 5

Conclusions

The electrochemical properties and behaviour of the oxygen non-stoichiometry in LiMn₂O₄ deposited on oxygen-conducting ZrO_2 (YSZ) were investigated under various external conditions using XRD measurements and electrochemical impedance spectroscopy. In situ XRD measurements were performed to assess the stability of the sample under high temperatures in both oxygen and nitrogen atmospheres. In an oxygen atmosphere, initial heating caused an expansion of the LMO lattice. Around 550 °C, the lattice parameter decreased due to oxygen release. Above 750 °C, the lattice distance increased again due to thermal expansion. This low-temperature behaviour was initially observed under a nitrogen atmosphere as well; however, at temperatures exceeding 700 °C, a phase transition of LiMn₂O₄ to Mn₃O₄, LiMnO₄, and oxygen occurred. In both atmospheres the thin film surfaces took on an amorphous appearance after heating to 1200 °C and subsequent cooling. Due to the behaviour observed in the nitrogen atmosphere, a maximum temperature of 620 °C was chosen for the electrochemical impedance spectroscopy (EIS) measurements.

Impedance measurements of samples with varying states of charge were conducted over a temperature range of approximately 373 °C to 618 °C. For all models considered, the capacitance increased as the temperature increased, while the resistance decreased. This behaviour of both properties is attributed to the increased concentration of ionic defects, such as oxygen vacancies or metal interstitials, at elevated temperatures. This trend, with only minor exceptions, holds true across all variations in oxygen partial pressure and lithium content of the samples.

The variation of oxygen partial pressure between 1 bar and 0.2 mbar reveals a correlation between gas phase and capacitance: as the oxygen partial pressure decreases, the capacitance increases. This relationship can be attributed to an increase in ionic defect concentration in response to the reduced oxygen content in the atmosphere. At the lowest oxygen partial pressures, the capacitance shows a more pronounced increase. With increasing temperature, the gradient in a log-log plot of the capacitance over the partial pressure increases and reaches a level around -0.2 for the different modelling of sample D1. Consequently, the maximum capacitance is observed at high temperatures and low oxygen partial pressures, a trend consistent across all models considered.

The capacitance behaviour of samples with different lithium contents is similar and notably stable across all parameters. At higher degrees of delithiation, the capacity is lower at high temperatures and high oxygen partial pressures. However, all samples except the highly overlithiated sample D2 converge to a similar range of magnitudes at lower partial pressures around 3200 F/cm^3 . This indicates an ionic defect concentration in the range of 10^{-2} with respect to lattice sites. For samples D3, D4 and D5 at the highest temperature of approximately 618°C, the gradient in the log-log plot approaches -0.35.

No such clear correlation was observed for the resistance over partial pressures and delithiation levels. The resistance varies less significantly, generally displaying a similar range of magnitudes at low temperatures across samples, except for sample D2 ($\delta = 0.48$) with a significantly lower resistance. At higher temperatures, particularly around 618 °C, a notable increase in resistance occurs as the oxygen partial pressure decreases. This resistance fluctuation is more pronounced at low partial pressures and reaches higher values for delithiated samples.

The lithium content of the samples can still be circulated after reaching the maximum temperature and minimum oxygen partial pressure in the EIS measurements. However, because the samples were not fully contacted within the delithiation cell and the aqueous electrolyte introduced side reactions due to the applied voltage up to 1.1 V relative to the Ag/AgCl reference electrode, a more precise comparison of charge cycles is challenging. Alternative sample configurations and cell designs would be necessary to better characterize this behaviour.

Appendix A

Directories

A.1 List of Illustrations

2.1	Classification of point defects.	5
2.2	Crytal structure of $LiMn_2O_4$	9
2.3	Charateristics of the different Warburg elements; semi-infinite Warburg W_I , open	
	Warburg W_o and closed Warburg W_s	13
3.1	Layer composition of the applied symmetrical sample geometry	15
3.2	EIS measurement setup: a) quartz sample holder, b) outer fused silica tube,	
	c) tube furnace, d) mass flow controllers with control unit, e) gas inlet and outlet,	
	f) thermocouple, g) grounding $\ldots \ldots \ldots$	19
3.3	Detailed view of the sample holder used for the EIS measurement: (a) quartz	
	sample holder, (f) thermocouple, (h) Pt contacts $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	19
3.4	Model 1: YSZ resistance in series with one R-CPE element	21
3.5	Model 2: YSZ resistance in series with two R-CPE elements	22
3.6	Model 3: Transmission line model with no surface resistance	22
4.1	X-ray diffraction patterns of LMO recorded at various temperatures under an	
	oxygen atmosphere, including the position of the two peaks considered from the	
	literature [36]	24
4.2	Displacement of the (111) peak (left) and the (222) peak (right) of the LMO	
	under nitrogen and oxygen atmosphere, across the temperature range from $25^{\circ}\mathrm{C}$	
	to 1200 °C	25
4.3	Variations of the lattice parameter of LMO under nitrogen and oxygen atmosphere $% \mathcal{A}$	
	determined from the (111) peak (left) and the (222) peak (right) measured in the	
	temperature range from $25 ^{\circ}$ C to $1200 ^{\circ}$ C	25
4.4	X-ray diffractions of LMO at different temperatures in an nitrogen atmosphere,	
	including the position of the two peaks considered from the literature [36]	26

APPENDIX A. DIRECTORIES

4.5	Displacement of the (111) peak of the LMO under nitrogen and oxygen atmo-	
	sphere, across the temperature range from $25 ^{\circ}$ C to $1200 ^{\circ}$ C	28
4.6	Variations of the lattice parameter of delithiated LMO under nitrogen and oxygen	
	atmosphere determined from the (111) peak measured in the temperature range	
	from $25 ^{\circ}$ C to $1200 ^{\circ}$ C.	29
4.7	SEM images at 80,000 \times magnification of the LMO layers with thicknesses of	
	$80\mathrm{nm}$ (left) and $160\mathrm{nm}$ (right), deposited on YSZ	29
4.8	SEM images at 10,000× magnification of the LMO layers with 160 nm after the	
	in situ XRD in ${\rm O}_2$ (left) and ${\rm N}_2$ (right) atmosphere, deposited on YSZ. $\ . \ . \ .$.	30
4.9	Comparison of XRD measurements in an oxygen atmosphere at 50 $^{\circ}\mathrm{C},~1200^{\circ}\mathrm{C}$	
	and 50 °C after reaching 1200 °C and rapid cooling	31
4.10	SEM image at $10,000 \times$ magnification of a delithiated LMO layer with 80 nm after	
	the in situ XRD in O_2 atmosphere, deposited on YSZ	31
4.11	Full impedance spectrum (right) and the YSZ-feature (left), with $T = 374$ °C,	
	$p_{O_2} = 200 \text{ mbar and } \delta = 0.87$	33
4.12	Deviation between the calculated and measured temperatures as a function of	
	ionic conductivity $\sigma_{\rm ion}$ at an oxygen partial pressure of $p_{O_2} = 200$ mbar and a	
	delithiation of $\delta = 0.87$.	33
4.13	Model 1: YSZ resistance in series with an R-CPE element	34
4.14	Model 2: YSZ resistance in series with two R-CPE elements.	35
4.15	Model 3: Transmission line model with no surface resistance	36
4.16	Comparison of the three models and the measurement for the temperatures a)	
	374 °C, b) 522 °C and c) 618 °C at an oxygen partial pressure of $p_{O_2} = 200 \text{ mbar}$	
	and a delithiation of $\delta = 0.87$	37
4.17	Temperature dependence of the capacitances (left) and resistances (right) fitted	
	from the three models at an oxygen partial pressure of $p_{O_2} = 200 \text{ mbar}$ and a	
	delithiation of $\delta = 0.87$.	38
4.18	Temperature dependence of the capacitances (left) and resistances (right) fitted	
	from the three models at an oxygen partial pressure of $p_{O_2} = 200 \mathrm{mbar}$ and a	
	delithiation of $\delta = 0.48$.	39
4.19	The Arrhenius plots for the resistances determined using Model 1 of the sample	
	D1 (left) and D2 (right) at an oxygen partial pressure of $p_{O_2} = 200 \mathrm{mbar.}$	40
4.20	The Arrhenius plots for the capacitance determined using Model 1 of the sample	
	D1 (left) and D2 (right) at an oxygen partial pressure of $p_{O_2} = 200 \mathrm{mbar.}$	41
4.21	Temperature dependence of the capacitor C_e in Model 3 (Figure 4.15) at an	
	oxygen partial pressure of $p_{\mathrm{O}_2}=200\mathrm{mbar}$ and a delithiation of $\delta=0.87.$	42
4.22	Oxygen partial pressure dependence of the capacitances determined using Model	
	1 for the different temperatures of sample D1 with a delithiation of $\delta=0.87.$	43

APPENDIX A. DIRECTORIES

4.23	Comparison of XRD measurements before and after the EIS measurement for D_{1} with a delithistic level of $\delta = 0.87$	4.4
	sample D1 with a delitination level of $\delta = 0.87$.	44
4.24	Temperature dependence of the capacitances fitted from the three models at an	
	oxygen partial pressure of $p_{O_2} = 1$ bar (left) and $p_{O_2} = 0.2$ mbar (right) with	
	$\delta = 0.87.\ldots$	45
4.25	Oxygen partial pressure dependence of the capacitances determined using the	
	three models for the temperatures of 618°C and 374°C of the sample D1 with	
	$\delta = 0.87.\ldots$	45
4.26	Gradient of capacitances across the full range of oxygen partial pressure for the	
	three models, shown as a function of temperature for the delithiation level $\delta=0.87.$	46
4.27	Oxygen partial pressure dependence of the resistances determined using Model 1	
	for the different temperatures of sample D1 with a delithiation of $\delta = 0.87$	47
4.28	Oxygen partial pressure dependence of the resistances determined using the three	
	models for the temperatures of 618 °C and 374 °C of the sample D1 with $\delta = 0.87$.	48
4.29	Oxygen partial pressure dependence of the capacitances determined using Model	
	1 for the different temperatures of sample D2 with a delithiation of $\delta = 0.48$.	50
4.30	Oxygen partial pressure dependence of the capacitances determined using Model	
	2 for the different temperatures of sample D2 with a delibility of $\delta = 0.48$	51
4 31	Temperature dependence of the capacitances (left) and resistances (right) fitted	-
1.01	from the three models at an oxygen partial pressure of $n_0 = 1$ mbar with $\delta = 0.48$	52
4 32	Oxygen partial pressure dependence of the capacitances determined using Model	01
1.02	3 for the different temperatures of sample D2 with a delibilitient of $\delta = 0.48$	53
4 33	Gradient of capacitances across the full range of oxygen partial pressure for the	00
1.00	three models shown as a function of temperature for the delithiation level $\delta = 0.48$	53
1 3/	Over partial pressure dependence of the resistances determined using Model 1.	00
4.04	for the different temperatures of sample D2 with a delithistion of $\delta = 0.48$	54
4.95	For the different temperatures of sample D_2 with a definitiation of $\theta = 0.46$	94
4.55	Oxygen partial pressure dependence of the resistances determined using the three models for the temperatures of 612 °C and 266 °C of the sample D2 with $\delta = 0.48$	FF
4.90	models for the temperatures of 612 °C and 500 °C of the sample D2 with $\theta = 0.48$.	99
4.30	Comparison of a cycle of the sample D3 ($\delta = 1.27$) in aqueous electrolyte with	FC
4.07	the discharge curve down to 0.9 v.	50
4.37	Oxygen partial pressure dependence of the capacitances determined using Model	
	1 for the different temperatures of sample D3 with a delithiation of $\delta = 1.27$	57
4.38	Oxygen partial pressure dependence of the capacitances determined using the	
	three models for the temperatures of 618 °C and 374 °C of the sample D3 with	
	$\delta = 1.27.\ldots$	58
4.39	Gradient of capacitances across the full range of oxygen partial pressure for the	
	three models, shown as a function of temperature for the delithiation level $\delta = 1.27$.	59
4.40	Oxygen partial pressure dependence of the resistances determined using Model 1	
	for the different temperatures of sample D3 with a delithiation of $\delta = 1.27$	59

APPENDIX A. DIRECTORIES

4.41	Oxygen partial pressure dependence of the capacitances determined using Model	
	1 for the different temperatures of sample D4 with a delithiation of $\delta=1.34.$	60
4.42	Oxygen partial pressure dependence of the capacitances determined using Model	
	3 for the different temperatures of sample D4 with a delithiation of $\delta=1.34$	61
4.43	Gradient of capacitances across the full range of oxygen partial pressure for the	
	three models, shown as a function of temperature for the delithiation level $\delta=1.34.$	62
4.44	Oxygen partial pressure dependence of the resistances determined using Model 1	
	for the different temperatures of sample D4 with a delithiation of $\delta=1.34.$	62
4.45	Oxygen partial pressure dependence of the resistances determined using Model 3	
	for the different temperatures of sample D4 with a delithiation of $\delta = 1.34.$	63
4.46	Oxygen partial pressure dependence of the capacitances determined using Model	
	1 for the different temperatures of sample D5 with a delithiation of $\delta=1.68.$	64
4.47	Gradient of capacitances across the full range of oxygen partial pressure for the	
	three models, shown as a function of temperature for the delithiation level $\delta=1.68.$	65
4.48	Oxygen partial pressure dependence of the resistances determined using Model 1	
	for the different temperatures of sample D5 with a delithiation of $\delta = 1.68.$	65
4.49	Oxygen partial pressure dependence of the capacitances determined using Model	
	1 for the temperatures of 618 $^{\circ}\mathrm{C}$ and 373 $^{\circ}\mathrm{C}$ with various delithiations	66
4.50	Gradient of capacitances across the full range of oxygen partial pressure for the	
	various delithiation levels, shown as a function of temperature. \ldots \ldots \ldots	67
4.51	Oxygen partial pressure dependence of the resistances determined using Model 1	
	for the temperatures of $618 ^{\circ}\text{C}$ and $373 ^{\circ}\text{C}$ with various delithiations	68
4.52	Temperature dependence of the capacitances(left) and resistances (right) at an	
	oxygen partial pressure of $p_{O_2} = 1$ mbar	70
4.53	Comparison of the current-voltage characteristics for the first two cycles of the	
	LMO thin film in aqueous electrolyte before and after the EIS measurements at	
	temperatures up to $T = 618^{\circ}$ C and $p_{O_2} = 0.2 \text{ mbar.} \dots \dots \dots \dots \dots \dots$	71

A.2 List of Tables

3.1	List of oxygen partial pressure $p_{\rm O_2}$ and their corresponding O_2, N_2 and 1 $\%$ O_2	
	flow rates	20
4.1	Lithium content of the examined samples measured by ICP-OES and the corre-	
	sponding voltage used for the delithiation process.	49

A.3 Bibliography

- S. Choi and G. Wang, "Advanced Lithium-Ion Batteries for Practical Applications: Technology, Development, and Future Perspectives," *Advanced Materials Technologies*, vol. 3, no. 9, pp. 1–21, 2018.
- [2] N. A. A. Qasem and G. A. Q. Abdulrahman, "A Recent Comprehensive Review of Fuel Cells: History, Types, and Applications," *International Journal of Energy Research*, vol. 2024, no. 1, pp. 1–36, 2024.
- [3] C. A. Rufino Júnior, E. R. Sanseverino, P. Gallo, M. M. Amaral, D. Koch, Y. Kotak, S. Diel, G. Walter, H.-G. Schweiger, and H. Zanin, "Unraveling the Degradation Mechanisms of Lithium-Ion Batteries," *Energies*, vol. 17, no. 14, pp. 1–52, 2024.
- [4] Y. Lyu, X. Wu, K. Wang, Z. Feng, T. Cheng, Y. Liu, M. Wang, R. Chen, L. Xu, J. Zhou, Y. Lu, and B. Guo, "An Overview on the Advances of LiCoO₂ Cathodes for Lithium-Ion Batteries," *Advanced Energy Materials*, vol. 11, pp. 1–29, 2020.
- [5] Y. Furushima, C. Yanagisawa, T. Nakagawa, Y. Aoki, and N. Muraki, "Thermal stability and kinetics of delithiated LiCoO₂," *Journal of Power Sources*, vol. 196, no. 4, pp. 2260– 2263, 2011.
- [6] W.-J. Zhang, "Structure and performance of LiFePO₄ cathode materials: A review," Journal of Power Sources, vol. 196, no. 6, pp. 2962–2970, 2011.
- [7] Y. Zhang, Q. Huo, P. Du, L. Wang, A. Zhang, Y. Song, Y. Lv, and G. Li, "Advances in new cathode material LiFePO₄ for lithium-ion batteries," *Synthetic Metals*, vol. 162, no. 13, pp. 1315–1326, 2012.
- [8] M. Thackeray, W. David, P. Bruce, and J. Goodenough, "Lithium insertion into manganese spinels," *Materials Research Bulletin*, vol. 18, no. 4, pp. 461–472, 1983.
- [9] J. Molenda, K. Swierczek, W. Kucza, J. Marzec, and A. Stoklosa, "Electrical properties of LiMn₂O_{4-δ} at temperatures 220–1100K," *Solid State Ionics*, vol. 123, no. 1, pp. 155–163, 1999.
- [10] T.-F. Yi, C.-L. Hao, C.-B. Yue, R.-S. Zhu, and J. Shu, "A literature review and test: Structure and physicochemical properties of spinel LiMn₂O₄ synthesized by different temperatures for lithium ion battery," *Synthetic Metals*, vol. 159, no. 13, pp. 1255–1260, 2009.
- [11] Q.-C. Zhuang, T. Wei, L.-L. Du, Y.-L. Cui, L. Fang, and S.-G. Sun, "An Electrochemical Impedance Spectroscopic Study of the Electronic and Ionic Transport Properties of Spinel LiMn₂O₄," *The Journal of Physical Chemistry C*, vol. 114, no. 18, pp. 8614–8621, 2010.

- [12] H. Xia, Z. Luo, and J. Xie, "Nanostructured LiMn₂O₄ and their composites as highperformance cathodes for lithium-ion batteries," *Progress in Natural Science: Materials International*, vol. 22, no. 6, pp. 572–584, 2012.
- [13] Y. Zhang, H. Xie, H. Jin, Q. Zhang, Y. Li, X. Li, K. Li, and C. Bao, "Research Status of Spinel LiMn₂O₄ Cathode Materials for Lithium Ion Batteries," *IOP Conference Series: Earth and Environmental Science*, vol. 603, no. 1, pp. 1–6, 2020.
- [14] N. Boaretto, I. Garbayo, S. Valiyaveettil-SobhanRaj, A. Quintela, C. Li, M. Casas-Cabanas, and F. Aguesse, "Lithium solid-state batteries: State-of-the-art and challenges for materials, interfaces and processing," *Journal of Power Sources*, vol. 502, pp. 1–34, 2021.
- [15] L. Ji, Z. Lin, M. Alcoutlabi, and X. Zhang, "Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries," *Energy Environ. Sci.*, vol. 4, pp. 2682– 2699, 2011.
- [16] M. Asadikiya and Y. Zhong, "Oxygen Ion Mobility and Conductivity Prediction in Cubic Yttria-Stabilized Zirconia Single Crystals," *Journal of Materials Science*, vol. 53, pp. 1699– 1709, 2018.
- [17] S. Badwal, "Stability of solid oxide fuel cell components," *Solid State Ionics*, vol. 143, no. 1, pp. 39–46, 2001.
- [18] S. P. Jiang, "Development of lanthanum strontium manganite perovskite cathode materials of solid oxide fuel cells: a review," *Journal of Materials Science*, vol. 43, pp. 6799–6833, 2008.
- [19] S. P. Jiang, "Development of lanthanum strontium cobalt ferrite perovskite electrodes of solid oxide fuel cells – A review," *International Journal of Hydrogen Energy*, vol. 44, no. 14, pp. 7448–7493, 2019.
- [20] A. L. Facci, V. Cigolotti, E. Jannelli, and S. Ubertini, "Technical and economic assessment of a SOFC-based energy system for combined cooling, heating and power," *Applied Energy*, vol. 192, pp. 563–574, 2017.
- [21] O. Chun, F. Jamshaid, M. Z. Khan, O. Gohar, I. Hussain, Y. Zhang, K. Zheng, M. Saleem, M. Motola, and M. B. Hanif, "Advances in low-temperature solid oxide fuel cells: An explanatory review," *Journal of Power Sources*, vol. 610, pp. 1–20, 2024.
- [22] A. E. Bumberger, S. Ražnjević, Z. Zhang, M. Kubicek, G. Friedbacher, and J. Fleig, "Chemical capacitance measurements reveal the impact of oxygen vacancies on the charge curve of LiNi_{0.5}Mn_{1.5}O_{4-δ} thin films," *Journal of Materials Chemistry A*, vol. 11, pp. 24072–24088, 2023.

- [23] S. S. Sharifi Asl, J. Lu, K. Amine, and R. Shahbazian-Yassar, "Oxygen Release Degradation in Li-Ion Battery Cathode Materials: Mechanisms and Mitigating Approaches," *Advanced Energy Materials*, vol. 9, pp. 1–19, 2019.
- [24] X. Hao, X. Lin, W. Lu, and B. Bartlett, "Oxygen Vacancies Lead to Loss of Domain Order, Particle Fracture, and Rapid Capacity Fade in Lithium Manganospinel (LiMn₂O₄) Batteries," ACS Applied Materials & Interfaces, vol. 6, pp. 10849–10857, 2014.
- [25] J. Wang, H. Xing, W. Hou, and Y. Xu, "Role of Oxygen Vacancies on the Performance of LiMn₂O₄ Spinel Cathodes for Lithium-Ion Batteries," *Physical Chemistry Chemical Physics*, vol. 25, p. 18903–18914, 2023.
- [26] J. Fischer, C. Adelhelm, T. Bergfeldt, K. Chang, C. Ziebert, H. Leiste, M. Stüber, S. Ulrich, D. Music, B. Hallstedt, and H. Seifert, "Development of thin film cathodes for lithium-ion batteries in the material system Li–Mn–O by r.f. magnetron sputtering," *Thin Solid Films*, vol. 528, pp. 217–223, 2013.
- [27] A. E. Bumberger, C. Boehme, J. Ring, S. Raznjevic, Z. Zhang, M. Kubicek, and J. Fleig, "Defect Chemistry of Spinel Cathode Materials: A Case Study of Epitaxial LiMn₂O₄ Thin Films," *Chemistry of Materials*, vol. 35, no. 13, pp. 5135–5149, 2023.
- [28] G. Job and F. Herrmann, "Chemical potential a quantity in search of recognition," European Journal of Physics, vol. 27, no. 2, pp. 353–371, 2006.
- [29] Z. Wang, J. Cai, Y. Han, T. Han, A. Chen, S. Ye, J. Liu, and J. Li, "Computational screening of spinel structure cathodes for Li-ion battery with low expansion and rapid ion kinetics," *Computational Materials Science*, vol. 204, pp. 1–7, 2022.
- [30] P. Piszora, "Inequality of quenched and high temperature structure of lithium deficient LiMn₂O₄," Journal of Alloys and Compounds, vol. 401, no. 1, pp. 34–40, 2005.
- [31] J. Schoonman, H. Tuller, and E. Kelder, "Defect chemical aspects of lithium-ion battery cathodes," *Journal of Power Sources*, vol. 81-82, pp. 44–48, 1999.
- [32] J. Fleig, "The grain boundary impedance of random microstructures: numerical simulations and implications for the analysis of experimental data," *Solid State Ionics*, vol. 150, no. 1, pp. 181–193, 2002. Ringberg Workshop 2000 Special Issue.
- [33] N. Laschuk, E. Easton, and O. Zenkina, "Reducing the resistance for the use of electrochemical impedance spectroscopy analysis in materials chemistry," *RSC Advances*, vol. 11, pp. 27925–27936, 2021.
- [34] T. Q. Nguyen and C. Breitkopf, "Determination of Diffusion Coefficients Using Impedance Spectroscopy Data," *Journal of The Electrochemical Society*, vol. 165, no. 14, pp. E826– E831, 2018.

- [35] J. Jamnik and J. Maier, "Generalised equivalent circuits for mass and charge transport: chemical capacitance and its implications," *Physical Chemistry Chemical Physics*, vol. 3, pp. 1668–1678, 2001.
- [36] K. Sato, D. Poojary, A. Clearfield, M. Kohno, and Y. Inoue, "The Surface Structure of the Proton-Exchanged Lithium Manganese Oxide Spinels and Their Lithium-Ion Sieve Properties," *Journal of Solid State Chemistry*, vol. 131, no. 1, pp. 84–93, 1997.
- [37] J. Kyu-Nam and P. Su-Il, "An Overview of Chemically/Surface Modified Cubic Spinel LiMn₂O₄ Electrode for Rechargeable Lithium Batteries," *Journal of the Korean Electrochemical Society*, vol. 9, no. 4, pp. 158–169, 2006.
- [38] V. Massarotti, D. Capsoni, and M. Bini, "Stability of LiMn₂O₄ and new high temperature phases in air, O₂ and N₂," *Solid State Communications*, vol. 122, no. 6, pp. 317–322, 2002.
- [39] H. Wulfmeier, D. Albrecht, J. Fischer, S. Ivanov, A. Bund, S. Ulrich, and H. Fritze, "Thin-Film Calorimetry: Analytical Tool for In-Situ Characterization of Lithium Ion Batteries," *Journal of The Electrochemical Society*, vol. 162, no. 4, pp. A727–A736, 2015.
- [40] A. Yamada, K. Miura, K. Hinokuma, and M. Tanaka, "Synthesis and Structural Aspects of $\text{LiMn}_2\text{O}_{4-\delta}$ as a Cathode for Rechargeable Lithium Batteries," Journal of The Electrochemical Society, vol. 142, no. 7, pp. 2149–2156, 1995.
- [41] Y. Ikuhara, X. Gao, R. Huang, C. Fisher, A. Kuwabara, H. Moriwake, and K. Kohama, "Epitaxial Growth of LiMn₂O₄ Thin Films by Chemical Solution Deposition for Multilayer Lithium-Ion Batteries," *Journal of Physical Chemistry C*, vol. 138, pp. 19540–19547, 2014.
- [42] M. Adamič, S. Talian, A. Sinigoj, I. Humar, J. Moskon, and M. Gaberscek, "A Transmission Line Model of Electrochemical Cell's Impedance: Case Study on a Li-S System," *Journal* of The Electrochemical Society, vol. 166, pp. A5045–A5053, 2018.
- [43] J. Sugiyama, T. Atsumi, T. Hioki, S. Noda, and N. Kamegashira, "Nonstoichiometry and defect structure of spinel LiMn₂O_{4-δ}," *Journal of Power Sources*, vol. 68, no. 2, pp. 641– 645, 1997.
- [44] J. Fleig, A. Schmid, G. Rupp, C. Slouka, E. Navickas, L. Andrejs, H. Hutter, L. Volgger, and A. Nenning, "The Chemical Capacitance as a Fingerprint of Defect Chemistry in Mixed Conducting Oxides," *Acta Chimica Slovenica*, vol. 63, pp. 509–518, 2016.