A scanning electron micrograph (SEM) showing a cross-section of a layered material. The top layer is dark grey and textured. Below it is a distinct horizontal band with three colors: purple on top, green in the middle, and blue on the bottom. The bottom-most layer is light grey and has a diagonal ribbed texture. The title text is overlaid on the top dark grey layer.

Interface-Engineering for All-Oxide Solid-State Batteries

T.A. Hendriks

INTERFACE-ENGINEERING FOR ALL-OXIDE SOLID-STATE BATTERIES

Theodoor Anton Hendriks

INTERFACE-ENGINEERING FOR ALL-OXIDE SOLID-STATE BATTERIES

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Cover:

The cover shows a Scanning Electron Microscope image of a cross-section of an All-Oxide Solid-State Battery thin film grown on a Nb:SrTiO₃-111 substrate. Manganese purple is used for the LiMn₂O₄ cathode layer, Lanthanum green for the Li_{3x}La_{2/3-x}TiO₃ electrolyte, and Titanium blue for the Li₄Ti₅O₁₂ anode.

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1 Introduction

1.1 Introducing batteries

Since their introduction in the 1990s, lithium ion (Li-ion) batteries have become the main power source for portable electronics and power tools applications. As society transitions towards electric and zero emission mobility, next generation electric cars require lithium batteries with superior energy and power density (respectively $Wh \cdot m^{-3}$ and $W \cdot m^{-3}$), without compromising safety and environmental concerns [1,2]. Also for stationary applications (such as grid stabilization and uninterruptable power supplies) lithium batteries become more popular due to their high energy and power density [3].

Energy density is the amount of energy (usually Wh) a certain volume or weight contains. Power density is the rate of energy flow a volume is capable of. An example of power density differences can be given by how fast a battery can be charged or discharged. At high power densities a car or electric motorcycle can be quickly charged or can have high power outputs and quickly accelerate. Two examples are shown in figure 1.

Figure 1, A popular electric car brand concept car and an electric motorcycle both exceeding speeds above 200 km/h. These high speeds are possible through the high power density and therefore output of their respective batteries.

There are many energy storage technologies available and under research. The main difference being their specific energy density as shown in figure 2 [4]. Super capacitors are known for their ability to quickly charge and discharge, and thus give off a lot of power. However, their energy density is limited. Lead acid is still largely used in car industry as the standard for starting, lighting and ignition power source. The Nickel-Cadmium (Ni-Cd) chemistry is widely known for its use in the old rechargeable batteries and as battery packs in electric tools. However, as Ni-Cd batteries suffer from memory effect, where the last discharge capacity is “remembered” and a consecutive use cannot discharge beyond this point, the Nickel Metal Hydrate (Ni-MH) chemistry does not. With the addition of a higher energy density, Ni-MH has taken the place of Ni-Cd. The Sodium Nickel Chloride chemistry Na / NiCl₂ is to the author’s knowledge not widely used. As it functions on higher temperatures this might be the main reason for the limited application of this chemistry in everyday appliances.

Figure 2, Battery technologies in terms of specific power density (W/kg) and energy density (Wh/kg). Adapted from [4]

The main reason for the popularity of lithium lies within its high energy density since it is the most electropositive (-3 V versus hydrogen) as well as the lightest metal (6.94 g/mol and 0.53 g/cm³) [5]. Batteries that are based on a lithium chemistry where the lithium ion is transported back and forth within the cell are so-called Li-ion batteries (rocking chair technology). The general build-up of such a li-ion battery is shown in figure 3. A cell consists of at least 5 parts: an anode, an electrolyte, a cathode, a current collector for the anode and the cathode, and a housing that contains these parts.

Figure 3, Working principle of a rechargeable lithium-ion battery. Upon discharge Li^+ -ions travel from anode to cathode through electrolyte while electrons travel outside the cell from anode to cathode powering anything in between. Upon charge Li^+ -ions are pushed from cathode to anode by an external force that supplies the electrons. Adapted from [6].

At their introduction in the '90s the common materials used for the anode and cathode were graphite and LiCoO_2 . As electrolyte, a liquid was used. This is often LiPF_6 dissolved in

EC:DMC with additional additives to influence the reactions that take place within this acidic medium and on the anode and cathode. When the liquid electrolyte gets into contact with the anode and/or cathode an interphase between the two is often (not always) created. This interphase consists of electrolyte components that have degraded and reacted partly with the electrode, forming a solid layer. Therefore, this layer is called a Solid-Electrolyte-Interphase layer, or SEI-layer for short.

Within the packaging of a cell, a separator is needed to avoid contact between anode and cathode when a liquid electrolyte is used. This takes up space and therefore decreases energy density. However, when this separator is made too thin, and a connection between anode and cathode is made (a short), it often causes a dramatic failure of the cell. Furthermore, during battery misuse or sometimes over the lifetime of a battery, dendrites are forming. The dendrites consist of metallic lithium and can sometimes penetrate the separator causing a short and therewith irreparable damage to the cell.

During discharge Li^+ -ions from the anode move towards the cathode while the material/metal (M, usually a transition metal) at the cathode is reduced from M^n to M^{n-1} . Upon charging a reversal process is forced; the material at the cathode goes back from M^{n-1} to M^n and the Li^+ -ion moves towards the anode. An example reaction scheme can be seen below:

In the reaction scheme the same materials as in figure 3 are used. There are, however, many more materials available, not only for the cathode and anode, but also the electrolyte. The ‘challenge’ in industry is finding the right combination with the right additives to design the best battery for a certain application. This has led to the common chemistry where a graphite anode is used with LiPF_6 as salt in the electrolyte and a cathode consisting of LiCoO_2 [6]. While other anodes such as Silicon, Li-metal and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exist, they contain more limitations than the standard used graphite Li_xC_6 . Silicon suffers from large volume changes during charge-discharge, causing loss of connection with the electrode and trapping of Li^+ . Li-metal is very reactive, causing decomposition of the electrolyte and making the battery unsafe. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a very stable anode, but due to its high potential vs. Li (~ 1.5 V) the voltage of the battery is much lower, decreasing the energy density. For the electrolytes, the LiPF_6 salt offers the highest ion-mobility while the organic compounds it is dissolved in (EC:DMC) offers a large enough stability versus the reactive conditions inside the cell, providing a reasonable safe battery. Therefore, the materials mentioned above (graphite, LiPF_6 and LiCoO_2) are the industry standard [6]. For the cathode, mostly intercalating materials are used. In these materials the Li^+ -ion can travel within the material’s framework. The three major materials are the olivine LiFePO_4 , the layered LiCoO_2 and the spinel LiMn_2O_4 (figure 4).

Due to the differences in their lithium diffusion pathways (which influence the lithium diffusivity through the materials) the three materials shown can behave differently with respect to their orientation. Limited diffusion pathways can influence the cycle-life and lifetime, which are dependent on the nature of the interphases between the electrodes and electrolyte. Furthermore, safety is a function of the stability of the electrode materials and their interfaces with the electrolyte [8 – 10].

Figure 4, The structure and lithium diffusion pathways are shown for three major intercalation cathode materials; the olivine LiFePO_4 , the layered LiCoO_2 and the spinel LiMn_2O_4 . Adapted from [7].

Existing batteries, using conventional layered oxide cathodes are not only reaching their power and energy density limits, but their application in electric mobility and large applications is also limited by their inadequate cycle life and inherently poor safety features [11].

LiCoO_2 allows for fast Li-diffusion combined with a high energy density of 272 mAh/g with a voltage of 4 V. However, for structural stability reasons only about half that energy density can be used (140 mAh/g). Furthermore, Co is expensive and environmental unfriendly [5].

On the other hand, the spinel LiMn_2O_4 , is a promising cathode material for next generation lithium batteries [12,13] due to its relatively high operating voltage (4.1 V vs Li) and

comparable energy density (theoretically 148 mAh/g, typical 125 mAh/g) combined with low cost and absence of direct environmental or safety hazards. Table 1 below shows the three major cathodes with their specific capacity (and practical capacity), average potential and (practical) energy density.

Framework	Compound	Specific Capacity [mAh g ⁻¹]	Average Potential [V vs Li ⁰ /Li ⁺]	Energy Density [Wh kg ⁻¹]
Layered	LiCoO ₂	272 (140)	4.0	1088 (560)
	LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂	272 (200)	4.0	1088 (800)
Spinel	LiMn ₂ O ₄	148 (125)	4.1	607 (513)
	LiNi _{0.5} Mn _{1.5} O ₄	148 (125)	4.7	696 (588)
Olivine	LiFePO ₄	170 (160)	3.45	587 (552)
	LiFe _{1/2} Mn _{1/2} PO ₄	170 (160)	3.4/4.1	638 (600)

Table 1, Comparison of multiple material compounds and their capacities, potentials and energy densities. Adapted from [7]. Values in brackets are numbers that are achieved in practice.

As the energy density of LiCoO₂ (560 Wh/kg) achieved in practice is comparable to that of LiMn₂O₄ (513 Wh/kg) with LiMn₂O₄ being cheaper, safer and more environmental friendly it is clear why it is a promising material [7]. However, compared to the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) the energy density is much lower while NCM uses less cobalt. On the other hand, the NCM is still costly and less safe than LiMn₂O₄ [12,13].

In the spinel LiMn_2O_4 (space group $\text{Fd}\bar{3}\text{m}$), lithium (Li) and manganese (Mn) occupy tetrahedral (8a) and octahedral (16d) sites in the intervening cubic close-packed array of oxygen (O) atoms (32e sites). The crystal structure is shown in figure 5b.

Figure 5, a) Characteristic ~ 4 V plateaus of LiMn_2O_4 cathode material versus Li-metal upon charge and discharge. b) Crystal structure of the spinel LiMn_2O_4 . c) The change of the lattice parameter of $\text{Li}_x\text{Mn}_2\text{O}_4$ over lithium content. At $x=0$ the cathode is charged, the voltage is above the 2 plateaus and the lattice parameter is around $8.05 \text{ \AA}$. c) is adapted from [7].

The edge-shared octahedral Mn_2O_4 host framework provides structural stability and interconnects face-shared tetrahedral lithium (8a) sites and empty octahedral (16c) sites. These interconnected pathways allow the three-dimensional diffusion of lithium-ions within the Mn_2O_4 framework, making LiMn_2O_4 suitable for high power applications. The lithium (de)intercalation at (8a) tetrahedral sites results into the characteristic ~ 4 V voltage plateaus (figure 5a) without distorting the spinel symmetry. Interestingly, this Mn_2O_4 framework can further host lithium into empty octahedral (16c) sites, resulting in a 3 V voltage plateau, almost doubling its capacity. Where the theoretical capacity of LiMn_2O_4 is 148 mAh/g, intercalating a second lithium ion increases the theoretical capacity of $\text{Li}_2\text{Mn}_2\text{O}_4$ to 288 mAh/g. While intercalating the second lithium ion the spinel undergoes a cubic to tetragonal phase transition (figure 6). This transition makes the cubic-spinel, with a lattice parameter of 8.25 Å, transform to a tetragonal spinel with lattice parameters of 9.24 Å $\cdot$ (5.65 Å)².

Figure 6, Discharge profile when including the 3 V plateau together with the crystal structure throughout lithiation. Inset crystal structures are adapted from [15].

Also interesting is the possibility to increase the operating voltage to ~5 V by partially substituting Mn with Ni in the Mn_2O_4 framework to achieve a $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ framework [14].

However, despite these advantageous properties, LiMn_2O_4 cathodes suffer from fading capacity and poor cycle life performance [16]. The origin of this capacity loss is attributed to two factors: first, the onset of Jahn-Teller distortion in deeply discharged electrodes [1,5,17,18], and second, the dissolution of Mn ions from the Mn_2O_4 framework [19]. The Jahn-Teller distortion, accompanied by the cubic to tetragonal phase transition, irreversibly damages the structural integrity of the spinel framework during deep cycling below ~3 V and causes permanent capacity loss. However, this Jahn-Teller distortion can be avoided by limiting the charging and discharging to the ~4 V plateaus. Mn dissolution causes continuous loss of active material and consequently blocking of 3D lithium diffusion pathways, thereby impeding the overall cell performance and remaining the key limitation for using LiMn_2O_4 cathodes [2]. Previous studies have suggested that acidification of electrolyte, caused by reaction of the lithiumhexafluorophosphate (LiPF_6) salt in electrolyte with H_2O , coupled with oxygen loss at the cathode surface, to be the origin of Mn dissolution [8,9,19]. The underlying mechanism can be understood via a disproportionation reaction of Mn^{3+} generating soluble Mn^{2+} :

Various strategies have been suggested to mitigate the Mn dissolution of LiMn_2O_4 , such as aliovalent doping, surface coating, nanostructuring, mixed phase synthesis [8,10 – 13,15, 16,20 – 26]. Although these strategies have indisputably shown significant enhancement in LiMn_2O_4 performance, it remains far from the desired level for usage in applications. However, studies have shown that the specific crystal facet in contact with the electrolyte plays an important role in the electrochemical reactions occurring at the cathode surface for

single crystalline nanowires [27], truncated structures [28], and thin films [29]. Highly controlled thin films make excellent model systems to study the lithiation mechanisms, as well as to elucidate the possible limiting factors, including Li-ion diffusion, Li-ion transport, and electronic transport. Epitaxial engineering is applied in **Chapter 2** to control the crystal orientation of LiMn_2O_4 thin films by growing on different oriented Nb:SrTiO_3 substrates. This enables a unique insight into the relation between electrochemistry, interface and crystal directionality, not obtainable in single crystals or polycrystalline samples, and previously not fully explored for epitaxial films [30 – 33].

Even though this material is considered a 3-dimensional material (i.e. lithium and electrons can move in 3 directions) interactions with the electrolyte and the substrate can be different for the different planes of the LiMn_2O_4 crystal. The surface of the cathode and anode interact with the electrolyte, the reaction products of which form a solid-electrolyte-interface (SEI). The different surface-planes of LiMn_2O_4 react differently with the electrolyte [29], however, detailed knowledge on this is limited. Therefore, in **Chapter 3** this electrochemical behavior of the cell is modeled in detail by Electrochemical Impedance Spectroscopy (EIS) to get more in-depth knowledge of the electrochemical response of each layer within the cell. Subsequently, for thorough understanding of LiMn_2O_4 its behavior under different loads and over time is elucidated in **Chapter 4**.

For LiMn_2O_4 it is known that the Jahn-Teller distortion at ~ 3 V causes rapid capacity loss due to the structural change from cubic- to tetragonal-spinel, damaging the framework and making material lose connection to the electrode. This is avoided by limiting the potential window to around 4 V. However, when the cell is allowed to further discharge to below 3 V, the capacity of the cathode can double. Looking back at table 1 and incorporating the additional discharge to $\text{Li}_2\text{Mn}_2\text{O}_4$, the energy density values show an interesting increase:

Framework	Compound	Specific Capacity [mAh g ⁻¹]	Average Potential [V vs Li ⁰ /Li ⁺]	Energy Density [Wh kg ⁻¹]
Spinel	LiMn ₂ O ₄	148 (125)	4.1	607 (513)
t-Spinel	Li ₂ Mn ₂ O ₄	288 (245)	4.1/3	1027 (873)

Table 2, Comparison of cubic-spinel LiMn₂O₄ to tetragonal-spinel Li₂Mn₂O₄. The capacities, potentials and energy densities are shown with numbers achieved in practice within brackets.

Adapted from [7].

As energy density is such an important feature in batteries, the electrochemical response of the additional discharge to Li₂Mn₂O₄, with a focus on structure stability and the proposed rapid capacity loss is studied in **Chapter 5**.

Next to energy density, power density plays a crucial role in the performance and safety of a battery. An important role is laid out here for the electrolyte. For liquid and gel electrolytes more literature is already available and these electrolytes are already widely used in commercial batteries. With regard to safety, a comment has to be made that for the gel and liquid electrolytes a separator is needed to avoid an internal electronic connection between the anode and cathode (a short) as this quickly discharges the battery and creates a lot of heat in the process. This heat can cause components of the electrolyte to start to decompose, react and add to the heat, causing a thermal runaway. Furthermore, the electrolyte together with the separator take up room but do not contribute to the total energy density. Therefore, the thinner the separator the better. Currently, the separator is usually made out of plastics such as polypropylene and polyethylene (PP & PE) and has a thickness of 10-25 μm [1].

A promising alternative comes from the use of solid-state electrolytes. These do not need the separator due to their inherent structural integrity. Therefore, the electrolyte can be made

thinner, to the point of it being a (nano)coating for the anode and/or cathode. As the electrolyte can be made thinner, the room used for materials contributing to the energy density is maximized. Furthermore, solid-state electrolytes are safer due to their stability at higher temperatures, but are often said to suffer from lower ionic conductivities and lower chemical and electrochemical stability windows [34]. However, the lower ionic conductivity is partly negated by a higher transference number, and recent research also shows larger stability windows [35].

Epitaxial systems of the cathode and electrolyte allow for model systems, which subsequently allow to research the link between interfaces and the electrochemical response with, in addition, also the lithium diffusion pathways. Therefore, in **Chapter 6**, first the model LiMn_2O_4 systems will be combined with the well-known and state-of-the-art solid-state electrolyte ($\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$), after which also the anode material ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is included to create full-solid-state epitaxial thin film batteries.

This allows for model epitaxial ceramic battery systems, which are currently unavailable.

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2 Orientation dependence in epitaxial engineered LiMn_2O_4 model systems

This Chapter is based on the publication:

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2.1 Introduction

Spinel LiMn_2O_4 has emerged as a promising cathode material for next generation lithium batteries [1,2] due to its relatively high operating voltage (4.1 V vs Li) and comparable energy density (theoretically 148 mAh/g, typical 120mAh/g) combined with low cost and absence of direct environmental or safety hazards. As mentioned in chapter 1, the edge-shared octahedral Mn_2O_4 host framework provides structural stability and the pathways within the framework allow the three-dimensional diffusion of lithium ions. The Mn_2O_4 framework can further host another lithium-ion, resulting in a 3 V voltage plateau, thereby almost doubling its capacity (theoretical capacity of $\text{Li}_2\text{Mn}_2\text{O}_4$ is 288 mAh/g) while the framework undergoes a cubic to tetragonal phase transition. Furthermore, by partially substituting Mn with Ni in the Mn_2O_4 framework the operating voltage of LiMn_2O_4 can be increased to ~5 V [3].

Despite this, the LiMn_2O_4 cathode suffers from a fading capacity and poor performing cycle life [4]. Two factors contribute to this: the dissolution of Mn ions from the Mn_2O_4 framework [8], and second, the onset of the Jahn-Teller distortion around 3 V for deeply discharged cells [5-7]. The distortion leads to a cubic to tetragonal phase transition that irreversibly damages the integrity of the spinel framework when the 3 V plateau is included in cycling, causing permanent capacity loss. By limiting the use to only the 4 V plateau, it can be avoided but only the theoretical energy density of 148 mAh/gram can then be achieved. Mn dissolution causes a continuous loss of active material and can block parts of the 3D lithium diffusion pathways, impeding the overall cell performance. This thereby remains the key limitation for using LiMn_2O_4 cathodes [9]. The origin of the dissolution is thought to be due to acidification of electrolyte, caused by a reaction of lithiumhexafluorophosphate (LiPF_6) salt in electrolyte with H_2O traces and coupled with oxygen loss at the cathode surface as explained through a disproportional reaction of Mn^{3+} generating soluble Mn^{2+} [8,10,11]:

A few strategies have been proposed to decrease the amount of Mn dissolution in LiMn₂O₄ such as aliovalent doping, surface coating, nanostructuring, and mixed phase synthesis [1-4,10,12-20]. Even though these methods have shown a significant mitigation of the Mn dissolution, and, consequently, enhancement in LiMn₂O₄ performance, it is not yet ready for usage in applications. Studies with single crystalline nanowires [21], truncated structures [22] and thin films [23] show that the specific crystal facet in contact with the electrolyte plays an important role in the electrochemical reactions occurring at the cathode surface.

Therefore, control of the interfacial properties between the electrodes and electrolyte is needed but remains a great challenge. Detailed understanding of the electrochemical behavior of specific crystal facets of battery materials can only be obtained when a single crystal orientation interfacing the electrolyte can be controlled. This requirement can be achieved by epitaxial thin film technology, in which the flat surface and restricted lattice plane of the thin film cathode can simplify the reaction mechanism at such highly ordered cathode-electrolyte interface as compared to an uncontrolled interface. Most studies on LiMn₂O₄ thin films have investigated polycrystalline samples, while only limited experimental research has been performed on single crystalline thin films [23-29]. Characterization of such epitaxial thin films has previously been focused on the structural properties, and only few reports have shown electrochemical properties by clear redox peaks in the cyclic voltammetry, and discharge capacities of ~125 mAh/g with clear plateau regions in the charge-discharge curves [26,28,29]. Detailed insight into the relation between the specific crystal orientation towards the adjacent electrolyte and its electrochemical behavior has been lacking, which has hampered the development of high-quality LiMn₂O₄ cathode with high cyclability. Hirayama et al. concluded from surface X-ray diffraction

measurements that a solid-electrolyte interface (SEI) was present on both (111) and (110) surfaces, although the (110) surface was less stable and indicated a higher Mn dissolution [25]. So far the electrochemical performance was only reported for LiMn_2O_4 thin films grown on (111)-oriented SrTiO_3 substrates [26,29], where an additional Li_3PO_4 coating was added to prevent a phase transition of the surface region and to suppress Mn dissolution and desorption of oxygen from the surface.

Here, by structural engineering of stable and epitaxial LiMn_2O_4 thin films, the electrochemical properties can be controlled and enhanced as compared to polycrystalline samples. By changing the crystal orientation of the underlying single crystalline substrate ((100), (110) and (111)) we can control the specific orientation of the LiMn_2O_4 thin film and, therefore, the cathode surface towards the adjacent electrolyte. All three types of LiMn_2O_4 films exhibit surfaces exposing predominantly {111} crystal facets, the lowest energy state surface for this spinel structure, which results in dramatic differences in surface morphology with pyramidal, rooftop or flat features for respectively (100), (110) and (111) LiMn_2O_4 films. Interestingly, the (100)-oriented films exhibited the highest capacities, (dis)charging rates up to 33 C, and good cyclability over a thousand cycles, demonstrating enhanced cycle life without excessive capacity fading as compared to polycrystalline studies [15].

To research the relation between electrochemistry and crystal directionality, epitaxial engineering can be used. Controlling the crystal orientation of LiMn_2O_4 thin films will enable a unique insight into this relation, not obtainable in single crystals or polycrystalline samples.

Experimental LiMn_2O_4 thin films were grown by pulsed laser deposition (PLD) at 600 °C on conducting Nb-doped (0.5 wt%) single crystalline SrTiO_3 ((100), (110) and (111)) substrates from a sintered LiMn_2O_4 (20 wt% excess Li_2O) target, using a KrF excimer laser

operating at 248 nm and at a repetition rate of 2 Hz. Flat Nb-SrTiO₃ substrates (5x5x0.5 mm³) with step terrace structure with unit cell height differences were obtained by annealing at 950 °C for 1.5 h in an oxygen flow of 150 ml/min. The oxygen pressure during growth was 0.2 mbar, while the laser energy fluence was 2.3 J cm⁻². After deposition, the thin films were slowly cooled down to room temperature in an oxygen pressure of 0.2 mbar at a rate of 10 °C min⁻¹. 7200 pulses resulted in a layer of roughly 100 nm as determined by cross-section SEM.

All LiMn_2O_4 (LMO) thin films were deposited under the same conditions and have a thickness of ~110 nm. A 50 nm SrRuO₃ (SRO) layer was deposited as an intermediate layer to enhance the electrical transport between the LMO cathode and the conducting Nb:STO substrate [26].

2.2 Characterization of the grown LiMn_2O_4 layers

The structural quality of the LMO films was investigated by X-ray diffraction (XRD) analysis, as shown in figure 1a. The three types of LMO films grown on Nb:STO substrates with different orientations exhibit coherent growth in which the out-of-plane crystal orientation of the films is aligned with the orientation of the substrate. The LMO(111) and LMO(110) films exhibit a high epitaxial crystallinity, with a lattice parameter of ~8.25 Å, without any impurity phase, in good agreement with previous studies of LMO growth on STO(111) and STO(110) substrates [23,26]. This suggests that the PLD process parameters (e.g. temperature, pressure, laser energy density, target composition) were optimized successfully to minimize loss of volatile lithium during ablation, nucleation and growth. Interestingly, the LMO films with (100)-orientation show minor contributions of a secondary phase, although all three LMO films were grown during the same deposition procedure.

The extra peaks suggest the presence of a small amount of Mn_2O_3 with (400)-orientation [30], which has been previously investigated as a promising anode material [31]. However, in our case the coexistence of this lithium deficient phase could be due to the enhanced lithium volatility at the (100)-surface of LiMn_2O_4 [13].

2

The alignment of the out-of-plane crystal orientation for all types of LMO films suggests an epitaxial relation between the crystal structures of the deposited LMO films and the underlying Nb:STO substrates, although large differences exist between spinel LMO ($a = 8.25 \text{ \AA}$) and perovskite STO ($a = 3.90 \text{ \AA}$). A preferred orientation of the LMO films is confirmed by detailed analysis of the in-plane orientation by XRD for the (100)-oriented films. There, the (113)-peaks of the substrate (Nb:STO) align with the (226)-peaks of the LMO thin film confirming the epitaxial relation (figure 1b). A Reciprocal Space Map (RSM) of the same peaks shows that although the LMO thin film is aligned with the crystal orientation of the Nb:STO substrate, the LMO crystal structures has relaxed to its bulk parameters (figure 1c).

Figure 1, a) Out-of-plane XRD measurements of 110 nm LiMn_2O_4 epitaxial thin films on 50 nm SrRuO_3 -coated Nb-SrTiO_3 substrates with different crystal orientations: (100), (110) and (111). Nb-SrTiO_3 substrate peaks are indicated by $\square$, and SrRuO_3 are indicated by *, while minor contributions of Mn_2O_3 phase are given by $\bullet$. b) Overlapping Nb:SrTiO_3 (113)- and LiMn_2O_4 (226)-peaks while the substrate is rotated in-plane. c) Reciprocal Space Map of the Nb:SrTiO_3 substrate (113)-peak and the LiMn_2O_4 thin film (226)-peak.

The quality of the LMO films was further investigated by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) analysis, as shown in figure 2. The three types of LMO films grown on Nb:STO substrates with different orientations exhibit distinct surfaces due to the coherent growth in which the out-of-plane crystal orientation of the films is aligned with the orientation of the substrate. Furthermore, their surface features are in good agreement with the in-plane orientation shown above. The surface of the LMO(100) film

exhibits square-like structures with significant height differences (RMS = ~ 45 nm), which is in good agreement with previously observed octahedron spinel structures [22,32].

Figure 2, AFM (top) and SEM (middle) analysis of the surface morphology of 110 nm LiMn_2O_4 thin films on SrRuO_3 -coated Nb-SrTiO_3 substrates with crystal orientations (100), (110) and (111). SEM images are taken after extensive electrochemical cycling and subsequent cleaning of the surfaces. Schematics (bottom) are shown of the expected crystal facets for the different surface morphologies.

Such pyramidal spinel structures consist of $\{111\}$ -crystal facets on all four sides with an occasional presence of a truncated top of the pyramid exhibiting a (100)-crystal facet. The LMO(110) film forms a layer with rooftop-like structures and a lower surface roughness (RMS = ~ 5 nm), caused by the anisotropic nature of the (110)-plane which favors diffusion

of atoms along the $[\bar{1}10]$ direction as compared to the $[001]$ direction [33]. This results in elongated $\{111\}$ -crystal facets exposed on the surface, which are all aligned in the same direction. Finally, the LMO(111) film forms a layer with triangle-like structures exhibiting a very low surface roughness ($\text{RMS} = \sim 1.5 \text{ nm}$). The triangular shape corresponds to the (111) plane in a cubic structure, for which two different types of in-plane triangle orientations can be observed. Therefore, all three types of LMO films with different out-of-plane orientations ((100), (110) and (111)) exhibit surfaces exposing predominantly $\{111\}$ -crystal facets, which confirms that this is the lowest energy state surface of the spinel crystal structure [22].

2.3 Electrochemical characterization

To study the dependence of the lithium transport on the specific crystal orientation of the LMO, the films were transferred to an argon atmosphere glovebox ($<0.1 \text{ ppm}$ of H_2O and O_2) and placed on a hot plate for $\sim 10 \text{ min}$ at 125°C to remove any water content. Subsequently, they were positioned in an electrochemical EC-ref cell by EL-CELL and combined with a glass fiber separator of 1 mm thickness, 0.6 mL electrolyte with 1 M LiPF_6 in $1:1$ ethylene carbonate : dimethyl carbonate (EC:DMC) and a lithium metal anode. The electrochemical measurements were performed at 22°C using a BioLogic VMP-300 system in a two-electrode setup in which the samples were cycled galvanostatically between 3.6 and 4.5 V with currents of $1, 2, 5, 10, 20,$ and $50 \mu\text{A}$, corresponding to C rates of approximately $0.7, 1.3, 3.3, 6.6, 13,$ and 33 C , respectively. A potentiostatic period of 5 min is used to ensure complete charge or discharge before the next step.

Thin films fabricated by pulsed laser deposition typically exhibit densities very close to theoretical values with negligible porosity. Therefore, the mass of the samples has been determined by using the theoretical density of LMO (4.28 g/cm^3) together with the volume of the sample (thickness $\times$ 5 mm width $\times$ 5 mm length). Figure 3 shows charge-discharge

curves for the LMO films with different orientations ((100), (110) and (111)) for various currents (1-50 μA), resulting in (dis)charge rates in the range 0.7-33 C.

Figure 3, Charge-discharge analysis of 110 nm LiMn_2O_4 films with different crystal orientations ((100), (110) and (111)) for various currents (1, 2, 5, 10, 20 and 50 μA). A potentiostatic period of 5 min. is used to ensure complete charge or discharge before the next step.

The characteristic voltage plateaus for these epitaxial LMO thin films are in good agreement with bulk LMO charge-discharge profiles [1]. The total discharge capacity for the slowest rate of 0.7C was the highest for the (100)-oriented LMO film (~ 129 mAh/g), while the (110)- and (111)-oriented LMO films exhibit discharge capacities of respectively ~ 113 mAh/g and ~ 95 mAh/g. The large surface area of the (100)-oriented LMO film, caused by pyramidal surface morphology, is considered to cause enhanced lithium kinetics as compared to the other crystal orientations. The crystal facets on all films are predominantly (111), which eliminates any possible effect from local variations in crystal facets. The enhanced lithium kinetics for the (100)-oriented LMO films is also demonstrated by the large capacities still achievable during (dis)charging when using higher rates. The used high currents stress the material more and make the variations in lithium intercalation for the different crystal

orientations more pronounced. For currents of $20\mu\text{A}$ ($\sim 13\text{ C}$) the discharge capacities for the (110)- and (111)-oriented films drop to $\sim 50\text{ mAh/g}$, while the (100)-oriented film still exhibits double the capacity ($\sim 100\text{ mAh/g}$). The initial drop in discharge capacity after the first charge-discharge cycles may be attributed to anionic reaction occurring at upper voltage cutoff combined with irreversible dissolution of surface lithium and manganese [20]. All films show a slightly higher charge capacity compared to the discharge capacity due to SEI formation and Mn dissolution. However, the difference in charge-discharge capacities are within acceptable coulombic efficiency limits: $>80\%$ after the first and $>90\%$ after 25 cycles.

The rate dependence of the discharge capacity is shown in more detail in figure 4 for the LMO films with different crystal orientations. After the initial 20 charge-discharge cycles with 3.3 C the films are consecutively cycled at various rates in the range $0.7\text{ C} - 33\text{ C}$ before finishing the sequence with 50 cycles at 3.3 C .

Figure 4, Rate performance analysis of 110 nm LiMn_2O_4 thin films on SrRuO_3 -coated Nb-SrTiO_3 substrates with different crystal orientations ((100), (110) and (111)) for various currents, and corresponding C rates.

The results show the stability of the LMO films during substantial cycling, as well as the enhanced performance of the (100)-oriented film as compared to the other orientations.

Interestingly, at the highest rate of 33 C the (100)-oriented film still exhibits a capacity of about 84 mAh/g, while the capacities of the (110)- and (111)-oriented films have almost reduced to zero. The observed variation in surface area between the differently oriented films (about 50% more surface area for (100)-oriented films as compared to (110)- and (111)-oriented films, see figure 2), cannot explain this dramatic difference in lithium kinetics.

Although the conventional understanding of the Li diffusion in LiMn_2O_4 is three-dimensional in which the Li ions hop over the 8a and 16c sites along the interconnected pathways, these zigzagging chains form lithium diffusion channels in specific directions [34].

Previous studies have suggested that although the (111)-oriented facets exhibit the lowest surface energy [13,35] the (100)- and (110)-oriented facets are better aligned to the lithium diffusion channels, thus increasing discharge capacities and facilitating high rate capabilities [36].

Our results demonstrate that very stable LiMn_2O_4 thin films with {111}-surface facets exhibit much higher rate capabilities for the (100)-direction as compared to the (110)-direction. Theoretical modeling would provide detailed insight into the diffusion mechanism in which the ease of lithium diffusion through the bottleneck is studied. The triangular opening between the oxygen ions allowing Li-diffusion is formed at the contact face between the tetrahedron about 8a and the octahedron about 16c and depends on the displacement of the O atoms, which can vary in differently oriented epitaxial thin films.

2.4 Synthesis temperature

During synthesis, Reflective High-Energy Electron Diffraction (RHEED) can be used to inspect the growth at the surface of the thin film. While increasing the temperature, a phase-transition above 600 °C was observed for the thin film of LiMn_2O_4 on (100)-Nb:SrTiO₃ as shown in figure 5.

Figure 5, Reflective High-Energy Electron Diffraction (RHEED) image for a thin film of LiMn_2O_4 grown on (100)-oriented Nb:SrTiO₃ at 600 °C after which the temperature was increased to 615 °C.

This RHEED pattern furthermore shows that the surface of the film is rough, as 3D spots are observed. This is in accordance with the rough surface (pyramids) as seen in AFM and SEM of the (100)-oriented thin LMO film in figure 2. At high temperatures and low oxygen background pressures a phase-transition for the LMO can be expected to either Li_2MnO_3 or Mn_2O_3 [1,37]. Due to lithium evaporation at high temperatures it is expected Mn_2O_3 is formed, which is characterized in XRD of figure 1. As the transformation into Mn_2O_3 resulted in thin films that are no longer electrochemically active, syntheses of thin films of LiMn_2O_4 are performed at 600 °C.

2.5 Thickness Dependence

The capacity of the thin-film cathodes should follow a linear trend to the thickness of the layer for fixed substrate surface size and film density. The fixed area allows for the calculation of the theoretical capacity per nm through the theoretical energy density and the density of the material:

$$Capacity = Thickness * A * \rho_{mat} * \rho_{Emat}$$

Here, the capacity [mAh] is a function of thickness [m], area (A) [m²], material density (ρ_{mat}) [g m⁻³] and the material's energy density (ρ_{Emat}) [mAh g⁻¹],

2

As the other parameters can be regarded as constant, capacity becomes linear related to thickness. However, size effects like nano-confinement and diffusion limitations can play a role as function of thickness. As the choice of substrate can have a large influence on the structure of the thin film, its density may also be influenced. Due to lattice parameter mismatch, strain might be present in the film. Although we have observed relaxation in the reciprocal space map of figure 1c, films with reduced thicknesses could experience more strain. This strain and its relaxation can cause defects, such as Mn occupying Li sites, that could decrease the density or block lithium pathways, thereby decreasing the capacity.

Discharge capacities of samples are plotted versus their LiMn₂O₄ layer thickness in figure 6. Due to the destructive nature of determining the thickness, this is done after cycling. Due to possible Mn-dissolution, the measured layer thickness could be an underestimation of the actual thickness right after thin film growth. However, the stability of the electrochemical behavior indicates a negligible effect of Mn-dissolution for the LMO thin films.

The capacity over layer thickness shows a clear linear behavior although the slope is lower (114 mAh g⁻¹) compared to that of the theoretical maximum (148 mAh g⁻¹). Most studies in literature achieves an energy density of around 120 mAh g⁻¹ [4, 26, 38, 39]. Therefore, the observed trend of 114 mAh g⁻¹ is within the error margin of the thickness estimation through cross-section SEM analysis.

The 2nd degree polynomial trendline is added to approximate the effects of limited diffusion of the Li⁺-ion into the LMO.

Figure 6, Capacity as function of thin-film layer thickness. The capacities for different orientations are shown in colored marks. Trendlines are added as guide to the eye where both the polynomial and linear trendline mostly overlap on this scale. The theoretical maximum capacity line is added to the graph and is based on 148 mAh/g, 4.28 g/cm³ and a substrate size of 5x5 mm². Thicknesses are estimated through cross-section SEM analysis after cycling.

Fick's first law for one dimension states:

$$J = -D \frac{d\phi}{dx}$$

The diffusion flux (J) is in [mol m⁻² s⁻¹], the diffusivity (D) is in [m² s⁻¹] and the concentration gradient ($\frac{d\phi}{dx}$) is in [mol m⁻⁴].

As the film thickness increases, the time needed for lithium-ions to diffuse through it increases. However, as the charging current is kept constant at 5 μA throughout the thickness range, the time needed to fill the capacity follows a linear trend just as the increase in time

needed for lithium to diffuse. Therefore, a linear trend is logical until the diffusion changes drastically. As the observed capacity follows a linear trend in the thickness range of 20 – 220 nm the diffusivity is presumed to be constant within this thickness range.

2.6 Cycle life

The cycle life of such high-performance (100)-oriented LMO films was investigated for several cells during prolonged battery cycling at similar conditions, see figure 7. The electrochemical behavior of all four cells exhibited good uniformity with initial capacities of about 120-130 mAh/g, which still provided capacities of about 90 mAh/g after a thousand cycles. The stability of the voltage plateaus over the full thousand cycles is shown in figure 7a and 7b, and indicates the stable internal resistance during the complete prolonged cycling. Figure 7c displays the enhanced cycle life performance for (100)-oriented LMO films with significantly higher capacity and coulombic efficiency over thousand cycles as compared to previous studies on bulk and polycrystalline LMO for which the capacity drops below 80% within 50 cycles [4, 15].

2.7 Conclusion

In conclusion, structural engineering enables improved control over the electrochemical properties of LiMn_2O_4 thin films, which is unique for epitaxial thin films and cannot be obtained in single crystal or polycrystalline samples. Control of the specific crystal orientation of the LMO thin films resulted in dramatic differences in surface morphology with pyramidal, rooftop or flat features for respectively (100), (110) and (111) orientations. All three types of LMO films exhibit surfaces exposing predominantly {111}-crystal facets, which is predicted to be the lowest energy crystallographic surface for this spinel structure [13, 35].

Figure 7, Cycle life analysis of four 110 nm (100)-oriented LiMn_2O_4 thin films on SrRuO_3 -coated Nb-SrTiO_3 substrates. The evolution of charge-discharge (a) and cyclic voltammetry behaviors (b) are shown during prolonged cycling. c) The discharge capacity and coulombic efficiency are given for a thousand cycles. During the measurements a current of $5 \mu\text{A}$ was used, which provided a (dis)charge rate of 3.3 C .

Alignment to lithium diffusion channels allows the (100)-oriented LMO films to exhibit the highest capacities and (dis)charging rates up to 33 C . The capacities of the epitaxial layers follow an expected linear trend with their thickness when 114 mAh/g is assumed. Good cyclability over a thousand cycles is achieved, demonstrating enhanced cycle life without excessive capacity fading as compared to previous polycrystalline studies.

2.8 References

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3 Modeling the electrochemical behavior of LiMn_2O_4 thin film cathode

3.1 Introduction

It has been shown that the different surface-planes of LiMn_2O_4 react differently with the electrolyte [1], however, detailed knowledge on this is limited. How much does the LiMn_2O_4 -electrolyte interphase influence the rate performance for the different orientations of the cathode, the degradation over cycling and the observed capacity? Furthermore, what is the lithium diffusion coefficient and how does it compare to literature? By modelling the electrochemical behavior of the cell, focusing on the electrochemical response of each layer within the cell, this can be elucidated.

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In a simplified picture, the rate performance of the cell is linked to Ohm's law: as the discharge current increases so does the voltage drop as determined by the internal resistance. However, the diffusivity of the lithium-ions through the thin film cathode, SEI, and liquid electrolyte plays a crucial role in the rate performance. The internal resistance and the diffusivity can be relatively simple to determine. The total internal resistance can be calculated from the shift in the voltage plateau while charging and discharging at multiple current rates. The diffusivity can be calculated through techniques such as Cyclic Voltammetry, Potentiostatic Intermittent Titration Technique (PITT) and Electrochemical Impedance Spectroscopy (EIS).

The total internal resistance is composed out of many components as can be seen in table 1. However, it remains difficult to establish the components of the internal resistance. The values of components within the total internal resistance, especially with respect to the layers they are made up of, and how to control them, cannot be obtained with the voltage shift during charge-discharge. To get in-depth knowledge on the processes that take place in the differently oriented ((100), (110) & (111)) LiMn_2O_4 thin films cathodes, Electrochemical Impedance Spectroscopy (EIS) will be used.

Type of resistance	Internal resistance of cell (R_i = ionic resistance + electrical resistance + interfacial resistance)
Ionic	<ul style="list-style-type: none"> • Electrode (cathode and anode) particle • Electrolyte
Electrical	<ul style="list-style-type: none"> • Electrode (cathode and anode) particle • Conductive additives • Percolation network of additives in electrode • Current collectors • Electrical taps
Interfacial	<ul style="list-style-type: none"> • Between electrolyte and electrodes • Between electrode particles and conductive additives • Between electrode and current collector • Between conductive additives and current collector

Table 1, Components of the total internal resistance of the cell. Adapted from [2]

EIS allows to model the electrochemical cell in detail by separating the behaviors of the different layers and interphases in the time domain. This allows to understand the ionic and electronic processes taking place within the thin film cathode while it sits inside a cell. By measuring the current response for small AC voltage perturbations, at different frequencies while the system is in thermodynamic equilibrium, the impedance as a function of frequency can be analyzed. Furthermore, by measuring at multiple voltages, the electrochemical behavior as function of lithiation can be obtained. Initially, the cell's voltage is set to obtain thermodynamic equilibrium after which the system is perturbed with a 10 mV sinusoidal voltage of which the frequency is swept from 1 MHz down to 1 mHz.

It is important to stress that the system should be in thermodynamic equilibrium. The material / cell that is measured can have both linear and non-linear behavior that varies with time or is constant. For the analysis it is assumed that the system shows linear behavior and does not change over time. However, it is known that the battery cell changes over time and shows non-linear behavior: the voltage of a plateau depends on the applied current and the capacity depends on the current and the amount of material. Therefore, it is assumed that the non-linear behavior can be approximated by applying a small perturbation around a set

voltage, which allows to characterize the material's behavior around that voltage. Furthermore, each measurement is done fast enough to be able to assume the material / cell did not age while allowing enough time to reach equilibrium after a new set voltage. Lastly, the quality of the measurements is checked through the indicators given by the software (BioLogic's EC-Lab), which give a $>1\%$ error for frequencies above 0.6 Hz.

Figure 1 shows an EIS measurement with the simplest circuit that would physically behave similar to a battery cell. The relation between the real and imaginary parts of the impedance are shown in figure 1a. Where an arrow indicates the direction in which the frequency increases.

Figure 1, a) Measured Impedance in Nyquist diagram and, b), physical representation through an equivalent circuit. Adapted from [13].

In figure 1b an equivalent circuit (EQC) is developed to model the measured impedance. In this case it exists of two resistors ($R1$ and $R2$) and a capacitor ($C2$). The angular frequency (ω_c) indicates the time constant at which the real impedance component of the capacity ($C2$) equals that of the resistance ($R2$). However, other EQC's can be used to represent the same impedance results shown in 1a. The circuits shown in figure 2 have the same impedance as function of frequency, however have different physical representations.

Figure 2, Two equivalent circuits a) and b) that have similar impedance as function of frequency but different physical representations. Adapted from [13].

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As a real battery (cell) is much more complex, also more complex circuits will be used. The challenge then lies in finding a model that fits the measured impedance while being a correct physical representation. A few assumptions, however, can already be made.

1. There will be a resistance present already at the highest frequencies. This resistance is due to cables, different connections, electronic conductivity through the cell's external housing, conductivity through the substrate, and ionic conductivity through the electrolyte [2].
2. Furthermore, at the interface between the electrolyte and the cathode a double layer capacitance is formed. Adsorbed ions from the solution on the cathode form a double layer. The value depends on many factors as electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, and impurity adsorption [2-4].
3. Additionally, a resistance to lithium transport resides inside the film. Due to lithium needing to find a place inside the electrode one gets a resistance to charge transfer.

The total reaction inside the whole cell is a continuous process with a net flux of zero at equilibrium when the cell is not charged or discharged.

From the cathode, in the charging reaction, electrons leave the LiMn_2O_4 and Li^+ -ions diffuse into the electrolyte. Thus, charge is being transferred. This reaction has a certain speed which depends on the kind of reaction, the temperature, the concentration of the reaction products and the voltage. When the overpotential, η , is very small and the electrochemical system is at equilibrium, the expression for the charge-transfer resistance can be described by:

$$R_{\text{ct}} = \frac{RT}{nFi_0}$$

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Here, the charge transfer resistance (R_{ct} in $[\Omega]$) is determined by the gas constant (R in $[\text{J mol}^{-1} \text{K}^{-1}]$), the temperature (T in $[\text{K}]$), the number of electrons (n) involved, the Faraday constant (F in $[\text{C mol}^{-1}]$), and the exchange current (i_0 in $[\text{A}]$) [2-4].

The charge transfer resistance (R_{ct} / R_2) is electrically in parallel with the double layer capacitance (C_{dl} / C_2). Together with a constant resistance (R_1), that will be present even at high frequencies, this provides a circuit as shown in figure 1b with a semi-circle like impedance response as shown in figure 1a.

4. As both anode and cathode are present in the cell, it is expected that the double layer capacity and charge-transfer resistance occur twice. Whether both can be independently resolved depends on how much their values differ. It is expected that the lithium anode's charge transfer resistance is lower, as its kinetics are faster and its surface is larger in the cells [2].
5. Finally, a Finite Space Warburg can be expected. The Warburg is a model to describe semi-infinite diffusion. It can be used for the solid-state diffusion of Li into the bulk of a cathode (LiMn_2O_4). When an impermeable boundary, where the lithium-ions cannot penetrate, is present, the Finite Space Warburg describes the electrochemical behavior. As the lithium-ions from the electrolyte can go into the cathode, but not further into the substrate, this finite space Warburg is a good model to fit part of the thin-film cathode [14].

Figure 3, Describing the behavior of the LiMn_2O_4 thin film cathode. a) Physical schematic, b) circuit model, and c) impedance behavior as function of faradic and diffusion time constants. Black arrow indicates the increasing frequency direction and red arrow indicates an increasing Warburg contribution. Adapted from [13].

With the charge transfer resistances, double layer capacitances, and a finite space Warburg, a model can be made (figure 3) to fit the electrochemical behavior of the thin-film LiMn_2O_4 cathode which will provide detailed information about the internal components of the total internal resistances and the behavior of the cell and consequently the LiMn_2O_4 thin film cathode.

3.2 Experimental

As mentioned, thermodynamic equilibrium is important, and therefore each measurement must be performed within a limited time-scale. Therefore, the LiMn_2O_4 thin-film is charged to 4.5 V, kept constant for an hour to reach equilibrium after which the electrochemical impedance spectroscopy (EIS) was performed. At the voltage of 4.5 V, the cathode can be regarded as completely delithiated ($\lambda\text{-Mn}_2\text{O}_4$). During EIS the impedance was measured from 1 MHz to 1 mHz, with 10 points per decade on a log scale. For each point a perturbation

of 10 mV AC is applied where an average of the impedance is taken over 5 sinusoidal periods. To go through the different lithiation states of $\text{Li}_x\text{Mn}_2\text{O}_4$ (4.5 – 3.8 V), steps of 10 mV are taken while at each step the voltage is kept constant for 5 minutes to reach thermodynamic equilibrium. This is repeated until a voltage of 3.8 V is reached. The voltage range allows analyzing the impedance while the cathode transitions from $\lambda\text{-Mn}_2\text{O}_4$ to LiMn_2O_4 .

3.3 Results and Discussion

A typical impedance result for a LiMn_2O_4 thin film is shown in figure 4 with voltages and lithiation levels shown in the legend. When the applied voltage is lowered the impedance for low frequencies (<2 Hz) changes drastically.

Figure 4b shows the low impedance values at the high frequencies which do not change with lithiation level. At first glance the graph in figure 4a seems to exhibit only two semi-circles. However, when zooming in on the high frequencies (figure 5b) a third semi-circle can be observed. The three semicircles with a substrate / electrolyte resistance and a Warburg should provide a reasonable model to fit the data.

As the impedance changes with the voltage, a good model should be able to fit the impedance for the whole voltage range. Fitting the impedance with the used model is shown in figure 5a. This model is in accordance with literature [3-5] with an extra capacitance (Q4) added to fit all voltages. This is then used to fit the LiMn_2O_4 thin film cathode in a half-cell configuration over the voltage range of 4.5 to 3.8 V.

During fitting and simulating the EIS measurement, only a constant Warburg resulted in being able to fit over the full potential range of EIS measurements. As the low frequency tails in figure 4a show an incline of more than 45° and the Q4 value in figure 5c is fluctuating with the tails, it is clear that the added capacity (Q4) overshadows any change in Warburg through the voltages resulting in a constant value during fitting.

Figure 4, a) Impedance of the LiMn_2O_4 thin film cathode in Nyquist Diagram for multiple voltages. b) A zoom-in on the impedance at high frequencies (1 MHz – 10 kHz).

Figure 5, a) Equivalent Circuit of the fitted model with, b), the found Resistances and, c), Capacitances. R_1 and $Wd1$ are constant over voltage and their parameters are respectively 6.407Ω and 866.97Ω , 2.374 s .

The resistance due to cables, different connections, electronic conductivity through the cell's external housing, conductivity through the substrate, and ionic conductivity through the electrolyte [2] is taken as constant and is combined in the constant $R1$ value of 6.407Ω . Other parameters like $R2$, $R3$, $R4$, $Q1$, $Q2$ and $Q3$ are almost constant and only seem to fluctuate lightly, possibly with small changes in the temperature of the laboratory over the 2.5-day period of EIS measurement. Furthermore, small changes can also be partly attributed to SEI layer growth, and depletion or changes in the Electrolyte and/or dissolution of Mn.

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During the discharging of the battery cell, it is observed that $Q4$ (figure 5c) follows a certain trend to allow a fit of the low frequencies of the EIS measurement, resulting in the tail observed in figure 4a. This 'tail' for the low frequencies starts around $10 \text{ k}\Omega$ on the real impedances and seems to encompass the capacity of the thin film. Plotting the real and imaginary impedances for 0.01 and 0.1 Hz (figure 6) it is observed that they are lower in the range where lithiation of $\text{Li}_x\text{Mn}_2\text{O}_4$ takes place and therefore in the region of plateaus in the discharging of the LiMn_2O_4 thin film cathode.

Figure 6, a) Real and, b), imaginary impedances as function of voltage and lithiation level in $\text{Li}_x\text{Mn}_2\text{O}_4$. In grey the capacity as a function of voltage is shown.

This is in agreement with the classical equation for the charge transfer resistance [6, 7]:

$$R_{ct} = 1/fFk_0Ac_o^{0.5}c_R^{0.5}$$

Where the charge-transfer resistance (R_{ct}) equals 1 over (combined) the electrochemical constant (f), times the Faraday constant (F), the rate constant (k_0), the area (A) and the square root of the concentration of available oxidation (c_o) as well as reduction sites (c_R). The total amount of intercalation sites (c_T) is constant ($c_o + c_R = c_T$). When the concentration of reduction (c_R) or oxidation sites (c_o) approaches the total amount of intercalation sites (i.e. at discharged or charged state) the resistance rapidly increases. This is observed in figure 6a and 6b when the voltage is <3.9 or >4.2 V.

As Q_4 changes over voltage with a certain trend as shown in figure 5c it was tried to link this parameter to the actual capacity of the layer. The trend closely resembles the peaks observed in the derivative (dQ/dE) of a discharge over voltage measurement (figure 7).

Figure 7, Fitted Capacitance Q_4 (black) and measured derivative of a discharge voltage profile (dQ/dE) (red) over voltage.

Both Q4 and dQ/dE have an increasing slope around 3.9 V, a peak at 4 V, a trough at 4.06 V, another peak at 4.12 V and a downwards slope around 4.2 V. Due to their resemblance the capacity was determined by the area under the curve. Here, Q4 overestimates the capacity by about a factor of seven. It is possible that this overestimation arises from thermodynamic non-equilibrium due to the time-scale of the experiment. When more time is taken to reach a better equilibrium this overestimation should diminish.

3.4 Calculating the diffusion coefficient

Determining values for the Lithium diffusion kinetics are important in order to be able to compare the electrochemical response of the thin films to literature. The Warburg component in the model describes the solid-state diffusion of Li into the bulk of LiMn_2O_4 . This allows, with correct simulation and fitting, one to use it to extract the diffusion coefficient. The ‘Warburg slope’ has a linear response and can be described as [4]:

$$A_w = \left(\frac{dE}{dx} \right) \left(\frac{V_m}{\sqrt{2DzFA}} \right)$$

Where the slope of the electrode potential $\left(\frac{dE}{dx} \right)$ is the voltage curve vs. [Li] in $\text{Li}_x\text{Mn}_2\text{O}_4$, the molar volume of LiMn_2O_4 (V_m) is in $[\text{cm}^3 \text{ mol}^{-1}]$, the chemical diffusion coefficient (D) is in $[\text{cm}^2 \text{ s}^{-1}]$, the charge-transfer number (z) of the lithium is +1, the Faraday constant (F) is in $[\text{Ah mol}^{-1}]$, and lastly the electrode area (A) is in $[\text{cm}^2]$

The Warburg slope as shown above has a linear response to the change in one over the square root of the angular frequency ($\Delta\omega^{-1/2}$) [4]:

$$A_w = \left(\frac{dE}{dx} \right) \left(\frac{V_m}{\sqrt{2DzFA}} \right) = \frac{\Delta\text{Re}}{\Delta\omega^{-1/2}} = \frac{\Delta\text{Im}}{\Delta\omega^{-1/2}}$$

Where the change in real impedance (ΔRe) is equal to the change in imaginary impedance (ΔIm) for a change of the angular frequency ($\Delta\omega^{-1/2}$).

The diffusivity (D) can then be calculated. However, as a correct fit or simulation of the Warburg component can be difficult, and dE/dx is dependent on the current used, large errors are expected. Using the formula, the diffusivity for the voltages and lithiation levels given in figure 4 are shown in table 2. Although large errors are expected, the diffusivity trend follows the conductivity [6] and diffusivity [8] trend observed in literature.

Voltage	[V]	4.29	4.12	4.06	3.98	3.8
Li _x Mn ₂ O ₄	[x]	0	0.25	0.5	0.75	1
Diffusivity	[cm ² /s]	7.12 10 ⁻¹⁵	1.01 10 ⁻¹⁵	1.88 10 ⁻¹⁵	1.33 10 ⁻¹⁵	4.33 10 ⁻¹⁶

Table 2, Diffusivity determined through EIS for voltages and lithiation levels.

The diffusivity can also be calculated through Cyclic Voltammetry (CV) and Potentiostatic Intermittent Titration Technique (PITT). In contrast to the thermodynamic equilibrium during EIS, the system is dynamic during Cyclic Voltammetry, while during PITT the system is in transient mode. To compare the diffusivity results obtained through EIS, PITT was used.

3.5 PITT

Potentiostatic Intermittent Titration Technique (PITT) allows to calculate the diffusivity through the current behavior after very small steps in the potential are taken. The current can be described by Fick's first law:

$$I(t) = -D \frac{dC_{Li}(x, t)}{dx} \Big|_{x=0}$$

Where the chemical diffusion coefficient (D) is in [cm² s⁻¹] and the Li-ion concentration (C_{Li}) is at distance (x) into the solid thin film from the electrode / electrolyte interface in [cm] and at time (t) [s].

After each step the current behavior is measured for a fixed period. The diffusion of lithium can be modeled as a transport based on Fick's second law

$$\frac{\partial C_{Li}(x, t)}{\partial t} = D \frac{\partial^2 C_{Li}(x, t)}{\partial x^2}$$

The boundary condition for $x \rightarrow \infty$ is $\lim_{x \rightarrow \infty} C(x, t) = C^0$ where C^0 is the equilibrium concentration.

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The small potential step in PITT gives a current transient $I(t)$ (figure 8) with a relationship to t [9]:

$$I(t) = \frac{2QD}{L^2} \sum_{n=0}^{\infty} \exp\left(-\frac{(2n+1)^2 \pi^2 D t}{2L^2}\right)$$

Where the total charge transferred during the potential step (Q) is in [C] and the thickness of the electrode (L) is in [cm].

At long times (where $t \gg L^2 D$) the $I(t)$ can be approximated by [10]:

$$I(t) = \frac{2QD}{L^2} \exp\left(-\frac{\pi^2 D t}{4L^2}\right)$$

One can then derive the chemical diffusion coefficients (D) from the slope of $\ln(I(t))$:

$$D = -\frac{4L^2}{\pi^2} \frac{d \ln(I(t))}{dt}$$

Using potential steps of 10 mV the current is measured for 10 minutes with a range from 4.5 V – 3.8 V, using the last 5 minutes of current for the slope of $\ln(I(t))$ gives the diffusivity of lithium for the 4 V plateaus as shown in figure 10.

Figure 8, Current behavior after 10 mV potential step and $\ln(I(t))$ at 3.8 V.

Figure 9, PITT (black) and calculated diffusivity (red) over time and voltage.

The diffusivity throughout discharging varies over voltage but is around $4 \cdot 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. The diffusivity value found through EIS ($\sim 1 \cdot 10^{-15}$) is about an order of magnitude lower than that through PITT ($\sim 4 \cdot 10^{-14}$), however in accordance with the variations found in literature [3, 4]. The large difference between EIS and PITT is attributed to the large error in the capacity

found in EIS. This error effects the Warburg slope. PITT is therefore expected to give a more representative diffusivity of the thin film cathode.

Bulk diffusivity of LiMn_2O_4 is in the order of $10^{-11} - 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ [11]. This higher bulk diffusivity is explained through the large impedances found for the charge transfer to the electron conductor. Looking back to the values attributed to the SEI film on the LiMn_2O_4 thin film cathode and its charge transfer (R3 and R4 in figure 5) both are an order of magnitude higher with respect to polycrystalline thin films on a gold substrate [3] and a stainless steel substrate [4]. The SEI layer resistance might be lowered by improvements to the electrolyte, which is outside the scope of this research / thesis. It is known that the band alignment of the LiMn_2O_4 with respect to its current collector is crucial which has led to the introduction of a SrRuO_3 current collector layer for Nb:SrTiO_3 substrates [12]. As a large charge transfer resistance still exists this either suggests further optimization of SrRuO_3 is needed or SrRuO_3 (alone) is insufficient to decrease the internal resistance and allow improved charge- discharge rates needed for high power density applications.

3.6 Conclusion

The model fitted to the performed EIS measurements gives insight into the components of the internal resistance as well as the capacity of the cathode. A large resistance to charge transfer indicates improvements to the current collector needs to be made. The capacity is overestimated by a factor of 7, possibly due to non-equilibrium. A longer time to stabilize the voltage should diminish this. The LiMn_2O_4 -electrolyte interface is second in determining the rate performance, the high charge transfer resistance influences the rate performance most. As only (100)-oriented thin film is measured, solely a start is made into the analysis of the different orientations and LiMn_2O_4 -electrolyte interphase, and their effect on the rate performance, degradation over cycling and observed capacity. The Warburg slope used to calculate the diffusivity of the thin film gives a diffusivity following a similar trend to that

found in literature. By means of PITT the Li-diffusivity was also calculated and compared. EIS gives an order lower diffusivity than that calculated through PITT. The found diffusivity through PITT for epitaxial thin films of LiMn_2O_4 is an order of magnitude lower compared to polycrystalline thin films on a gold and stainless steel substrate. The high resistance for charge transfer is largely responsible for this, again suggesting improvements to the current collector are needed to allow decreased internal resistance of the thin film.

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4 Electrochemical behavior of LiMn_2O_4 thin film cathode during different loads, and through time

4.1 Introduction

Due to the continuously growing demand for enhanced performance of batteries, scientific and technological efforts have been focused on electrode materials with larger capacity, higher energy- and power density, reversibility and structural stability during charge/discharge cycles, faster ionic diffusion and electronic transfer at high charge/discharge rates, lower costs, higher safety, and usage of more environmental friendly materials and processes [1,2,3].

Furthermore, recent progression in electric and hybrid vehicles ((H)EVs) demands high power densities of the current battery systems [4] combined with high mileage and longevity. Existing battery applications in electric mobility and stationary storage are limited by their inadequate cycle-life and inherently poor safety features [5]. The cycle-life and lifetime depend on the used materials and their interfaces, with safety being a function of the stability of the electrode materials and their interfaces with electrolyte [6-8].

Spinel LiMn_2O_4 has emerged as a promising cathode material for next generation lithium batteries [9,10] due to its relatively high operating voltage (4.1 V vs Li) and good energy density (theoretically 148 mAh/g, and 120 mAh/g typically) as compared to 140 mAh/g typically achieved for LiCoO_2 . Its energy density can be further increased by partially replacing Mn by Ni to get the higher voltage cathode $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (~4.7 V). An overview of common cathode materials and their capacities, average potentials and energy densities is given in table 1.

As mentioned and shown in figure 4 and 5 of chapter 1, the edge-shared octahedral Mn_2O_4 host framework provides structural stability and interconnects lithium and empty sites (figure 5b Ch.1). These pathways allow three-dimensional diffusion of lithium ions within the framework, making LiMn_2O_4 suitable for high power applications.

Framework	Compound	Specific Capacity [mAh g ⁻¹]	Average Potential [V vs Li ⁰ /Li ⁺]	Energy Density [Wh kg ⁻¹]
Layered	LiCoO_2	272 (140)	4.0	1088 (560)
	$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$	272 (200)	4.0	1088 (800)
Spinel	LiMn_2O_4	148 (125)	4.1	607 (513)
	$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	148 (125)	4.7	696 (588)
Olivine	LiFePO_4	170 (160)	3.45	587 (552)
	$\text{LiFe}_{1/2}\text{Mn}_{1/2}\text{PO}_4$	170 (160)	3.4/4.1	638 (600)

Table 1, Overview of common cathode materials by their capacities, potentials and energy densities. Specific capacity between brackets (capacities) are values achieved in practice. Adapted from [11].

Despite these advantageous structural properties, LiMn_2O_4 cathodes suffer from capacity fading and poor cycle life performance [12], which is mostly attributed to dissolution of Mn-ions from the Mn_2O_4 framework in the 4 V region [13]. This dissolution causes continuous loss of active material and consequently blocking of 3D lithium diffusion pathways, thereby impeding the overall cell performance. This, therefore, remains the key limitation for using LiMn_2O_4 cathodes in commercial applications [3]. On the other hand, significant enhancement in LiMn_2O_4 performance has been shown by controlling the specific crystal facet in contact with the electrolyte. It plays an important role in the electrochemical reactions occurring at the cathode surface for single crystalline nanowires, [14] truncated structures [15] and thin films [4]. Therefore, as shown in Chapter 2, long cycle life is achievable for LiMn_2O_4 cathodes through control over the interface towards the electrolyte.

To achieve high power densities, it is important to study and compare the electronic and ionic conductivities.

As lithium needs to intercalate faster, the amount of spots it can reach in a certain time is limited by the ionic transport diffusion coefficients.

Framework	Compound	Electronic Conductivity [S cm ⁻¹]	Ionic diffusion coefficient [cm ² s ⁻¹]
Layered	LiCoO ₂	~10 ⁻⁴	~10 ⁻⁹
Spinel	LiMn ₂ O ₄	~10 ⁻⁶	~10 ⁻¹⁰
Olivine	LiFePO ₄	~10 ⁻⁹	~10 ⁻¹⁴

Table 2, Electronic conductivity and ionic diffusion coefficient of multiple cathode materials in bulk and at room temperature. Adapted from [11,16]

When operating a cell, its voltage (E) is usually lower than the standard voltage (E_0) due to potential drops caused by several factors such as thermodynamics, polarizations, and the internal resistance of a cell. Mathematically this is stated as:

$$E = E_0 - [(\eta_{ct})_a + (\eta_{ct})_c] - [(\eta_c)_a + (\eta_c)_c] - iR_i = iR$$

Where the standard cell potential (E_0) is in [V], the activation polarizations (charge-transfer overvoltage) at the anode and cathode (respectively $(\eta_{ct})_a$ and $(\eta_{ct})_c$) are in [V], the concentration polarizations at the anode and cathode (respectively $(\eta_c)_a$, $(\eta_c)_c$) are in [V], the cell operating current (i) is in [A], the internal resistance of the cell (R_i) is in [Ω], and the apparent cell resistance (R) is in [Ω].

The higher the apparent resistance, the larger the drop in voltage and the less the cell is suitable for high power densities. Therefore, it is important to measure the internal resistance (and its components) as done by Electrochemical Impedance Spectroscopy (EIS) in chapter 3, as well as to monitor the discharge capacity when cycling at different rates and over time. This will provide the needed information on the rate-dependent part of the capacity, and the capacity degradation over time with respect to capacity fade due to Mn-dissolution.

4.2 Experimental

Thin LiMn_2O_4 films with a thickness of about 100 nm were fabricated on (100)-oriented Nb:SrTiO_3 substrates through PLD and assembled in a glovebox as described in chapter 2. After a first charge to 4.5 V at 3 μA and cyclic voltammetry between 4.5 and 3.3 V the samples undergo 10 charge-discharge cycles between 4.5 and 3.6 V at 5 μA . After these initial cycles the samples are cycled at multiple currents to study shifts in voltage plateaus and capacities. The applied currents are in the sequence 5-10-2-1-5-10-20-50 μA with each current applied for 10 cycles. Most samples exhibit a capacity of about 1 μAh which corresponds to C-rates of 5-10-2-1-5-10-20-50 C.

After the rate tests, the samples are measured at currents of 5-10-2-1 μA with 50 cycles per step, to measure the cycle life. Several samples were extensively cycled at a single current of 5 μA to study the cycle life over a thousand cycles. Details on the electrochemical setup have been described in the Experimental Methods of Chapter 2.

4.3 Effect of current on potential plateaus of LiMn_2O_4 around 4V

As observed in chapter 2 the 4 V plateaus of LiMn_2O_4 shift at increasing currents. Similarly, a voltage drop during sequential discharging is observed when the discharging is done at higher currents (figure 1a). Furthermore, an increase of the voltage of the 4 V charge plateaus is observed for higher charge currents. These shifts are reversible and respond linear due to the internal resistance through Ohm's law. As the voltage and capacity during charge and discharge varies due to changes in the chemical potential upon (de)lithiation the relation between voltage and applied current is non-linear. However, using the first derivative of the discharge voltage plateaus where it is closest to zero, as well as a local maximum in the first derivative in between the two distinctive voltage-plateaus of LiMn_2O_4 , a linear trend can be fitted (figure 1a and 1b).

Figure 1, a) Discharge curves of epitaxial thin film of LiMn_2O_4 at different currents. Using the first derivative, squares note a minimum for Plateau 1, circles a local maximum for the Halfway points, and triangles a 2nd minimum for Plateau 2. b) Plateau 1, Halfway, and Plateau 2 voltage points versus current graph with a linear fit. c) Electrochemical Impedance measurement of a LiMn_2O_4 thin film at 4.13 V with an indication for the Warburg resistance point.

The first derivative points correspond roughly with the 25, 50 and 75% points in the state of discharge of LiMn_2O_4 . A linear fit through these points has an R value of 0.997 indicating a good fit. The observed trends have an average slope of around $-0.00196 \text{ V } \mu\text{A}^{-1}$ which, by applying Ohm's law, amounts to a resistance of 1960 Ω . Furthermore, when no current is applied the voltages (plateau 1: 4.124 V, halfway: 4.054 V, plateau 2: 3.969 V) correspond

to the intercalation voltages of respectively $\lambda\text{-Mn}_2\text{O}_4$ to $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$, pure $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$, and $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ to LiMn_2O_4 [17-19].

During Electrochemical Impedance Spectroscopy the Warburg (see also Chapter 3 and figure 1c) sets in around $2000\ \Omega$, this allows to link the modeled resistances ($R_{\text{substrate}} + R_{\text{SEI-films}} + R_{\text{ct}}$) to the observed total internal resistance of $1960\ \Omega$.

With the resistance known, the resistivity can be calculated through:

$$\rho = R \frac{A}{l}$$

Where the resistivity (ρ) is in [Ωcm], the resistance (R) is in [Ω], the area (A) is in [cm^2] and the length of the sample (l) is in [cm]. With the known values (resistance ($1960\ \Omega$), area ($5 \times 5\ \text{mm}^2$) and length ($117\ \text{nm}$) (specific thickness of the measured thin film cathode)) are known, the resistivity can be calculated to be $4.18 \cdot 10^7\ \Omega\ \text{cm}$.

The conductivity can then be calculated by taking the inverse of the resistivity:

$$\sigma = \frac{1}{\rho}$$

This leads to a conductivity of $2.39 \cdot 10^{-8}\ \text{S cm}^{-1}$, which is close to that found literature for polycrystalline LiMn_2O_4 thin films:

($100\ \text{nm}$, Au substrate of $10 \times 8\ \text{mm}^2$, $600\text{-}900\ \Omega$, $2.08 \cdot 10^{-8}\ \text{S cm}^{-1}$) [20]

($330\ \text{nm}$, stainless steel substrate, $10\ \text{mm}$ diameter, $500\ \Omega$, $8.35 \cdot 10^{-8}\ \text{S cm}^{-1}$) [21]

whereas the bulk conductivity of LiMn_2O_4 is around $1 \cdot 10^{-6}\ \text{S cm}^{-1}$ [16,22]. Looking back at the Impedance Spectroscopy in the previous chapter the difference in the conductivity with

literature can be mostly explained by the charge-transfer resistance ($\text{SrRuO}_3 - \text{LiMn}_2\text{O}_4$) and the SEI-film ($\text{LiMn}_2\text{O}_4 - \text{electrolyte}$).

The large charge-transfer resistance could indicate a high resistance for the Li-ions and/or electrons to reach a suitable intercalation spot which could be attributed to grain boundaries or, in the case of high electronic resistance, a problem at the interface between SrRuO_3 and LiMn_2O_4 . Although SrRuO_3 was already introduced to reduce the barrier between Nb:SrTiO_3 -substrate and LiMn_2O_4 [23], its quality will still influence the measured resistance. Furthermore, during Pulsed Laser Deposition there is a possibility of interfacial intermixing. The Mn_2O_3 -impurity phase as observed in chapter 2 could have partial intermixing of Ru from the SrRuO_3 into $\text{Li}_y\text{Ru}_x\text{Mn}_{2-x}\text{O}_3$, a phase that would also be electrochemically active [24, 25]. Although such interfacial layer would probably be very thin, it might influence the electronic conduction between the thin LiMn_2O_4 film and the substrate. This, therefore, requires more detailed investigation in future research and, in addition, demonstrates the importance of interface engineering.

4

4.4 Effect of current on the capacity

As the voltage plateaus drop for higher currents, and a cell exhibits higher internal resistances, the discharging of the cell is hindered. With a cut-off voltage of 3.6 V, the discharge plateaus of LiMn_2O_4 can fall below this voltage and the battery cannot be regarded as fully discharged ($x < 1$ for $\text{Li}_x\text{Mn}_2\text{O}_4$).

Also, due to increased voltage plateaus upon charging at higher rates the cell might not be fully charged ($x > 0$ for $\text{Li}_x\text{Mn}_2\text{O}_4$) at the cut-off voltage of 4.5 V. However, due to a constant voltage period of 5 minutes after charging, the cell should be fully charged before subsequent discharging. The same applies upon discharging, however, current due to a continued lithium intake during the constant voltage period is not taken into account.

Figure 2 gives, for a sequence of currents, an overview of the capacity, as well as the voltage and current behaviors over the capacity. For figure 2a the voltage profile as function of capacity for a sequence of currents can be observed, as well as an increase in the capacity (ΔC) during the voltage hold period of 5 minutes. As higher currents are used, the voltage plateaus shift below the 3.6 V cut-off voltage, decreasing the capacity with $V_{\text{cut-off}}$ as shown in 2c.

Figure 2, a) (Dis)charge profiles for a sequence of currents. b) Current behavior after $V_{\text{cut-off}}$ is reached. c) Capacities as function of cycle for the current sequence.

The increase in capacity during the voltage hold period becomes clearer in 2b, where the current over capacity is shown. Here the current is constant until the lower cut-off voltage is

reached. The period until 3.6 V is reached is shown in seconds, after this period the current decreases during the voltage hold of 5 minutes. Here, still some effect of the two voltage plateaus of LiMn_2O_4 can be observed as a change in current slope around 0.4 μAh takes place.

During the voltage hold nearly all the lithium is either inserted into (discharge) or extracted out of (charge) the thin LiMn_2O_4 film showing that the voltage hold period is nearly sufficient to obtain a full charge before subsequent discharge. The lower discharge capacity at high currents with $V_{\text{cut-off}}$ is, therefore, mostly due to the cut-off voltage in combination with the high internal resistance.

4.5 Electrochemical response through time

As not only the energy density but also the cycle life of a battery is important, the progressive decline of the electrochemical response over time while cycling the cell is measured. In the previous section the cycle life was measured while changing currents. However, as the charge and discharge rates might influence the degradation processes due to different internal resistances between samples, in this study the current was kept constant at 5 μA from the first cycle onwards. Four samples with equal thin LiMn_2O_4 films, synthesized at the same moment by Pulsed Laser Deposition, were used to, furthermore, check reproducibility. This is shown in figure 3. Here, both capacity and coulombic efficiency (the difference between the amounts of current that goes into the cell versus that which can be extracted) are shown for a thousand cycles, showing long cycle-life.

The four samples show some capacity degradation over their thousand cycles while their capacity over cycle graphs mostly overlap. Furthermore, after the first 20 cycles the coulombic efficiency is above 90%. This shows excellent reproducibility as well as good cyclability of the epitaxial thin LiMn_2O_4 films.

Figure 3, Capacity over cycles for four thin LiMn_2O_4 films grown on (100)-oriented Nb:SrTiO_3 substrates as well as their Coulombic efficiency of cycling.

The cycle-life performance of the synthesized thin LiMn_2O_4 films is compared to previous studies in bulk, as well as thin films, in figure 4.

Figure 4, Capacity over cycles for multiple LiMn_2O_4 cathodes from literature and this study's thin film (thick black line). *A coating was used to improve cycle-life. Please refer to table 3 (next page) for the cycling conditions used in these previous studies.

A clear decrease over cycles for all LiMn_2O_4 cathodes becomes apparent in the literature comparison in figure 4. The samples of J. Choa et al. [26] and Y. Cai et al. [27] are able to maintain higher capacity over cycles in the range 0-1000 cycles. However, these are for LiMn_2O_4 in particle form, not thin film. As particles have a reduced surface to bulk ratio, the dissolution of Mn is slower, adding to a slower decay of capacity over cycles. Furthermore, as the particles are usually sintered, they, too, exhibit mostly the energetically favored $\{111\}$ -facets. The thin film by M. Inaba et al. [28] has a lower starting capacity, but seems to have a lower capacity loss slope. As they do not show more than 100 cycles, however, the capacity retention over a longer period cannot be compared. Polycrystalline samples suffer more from internal stresses than large single crystalline particles, which can be observed for the capacity degradation of the samples of D.W. Shin et al. [29]. Discharge to lower voltages combined with higher rates both increase the existence of localized $\text{Li}_2\text{Mn}_2\text{O}_4$. Due to $\text{Li}_2\text{Mn}_2\text{O}_4$'s larger size, this induces more stress on the particles, and increased concentration of Mn^{3+} leads to increased Mn dissolution, leading to a quicker degradation [26].

A summary of the cycling conditions for the results shown in figure 4 is shown in table 3. From this it is concluded that the cycling conditions alone do not determine the capacity fade over cycles. Instead, due to the nature of the Mn dissolution through mainly the $\langle 110 \rangle$ surface as indicated in [4,14,15,32] the capacity fade over cycles is expected to be lower as more of the $\langle 111 \rangle$ facet is exposed to the electrolyte [26]. Structurally engineered thin films mostly exhibit their $\langle 111 \rangle$ surface, as well as particles sintered at high temperatures [26,27]. Polycrystalline particles [28,29] and particles that have a truncated shape [30] show multiple facets and, thereby, suffer more from the Mn dissolution.

Electrolyte	Ratio	Voltage range	C-rate	Cathode build-up		[ref.]
1M LiPF_6 EC:DMC	1:1	3.6 – 4.5	3.3	105 nm (100) LiMn_2O_4 on $\text{SrRuO}_3/\text{SrTiO}_3$	This study	
1M LiPF_6 EC:DMC	1:1	3.4 – 4.5	1	15 μm particles	J. Choa	[26]
1M LiPF_6 EC:DMC	1:1	3.5 – 4.3	10	Crystalline nanoparticles 150 nm	Y. Cai	[27]
1M LiClO_4 PC	1	3.5 - 4.25	~10	300 nm polycrystalline by PLD on Au	M. Inaba	[28]
1M LiPF_6 EC:DMC:EMC	1:1:1	3.5 – 4.5	0.5	2-5 μm particles *ZnO coating	S.B. Park	[30]
1M LiPF_6 EC:DMC	2:1	2.5 – 4.5 (only 4V peaks)	0.2	~10 μm particles	A. Blyr	[31]
1M LiPF_6 EC:DMC	1:1	3.0 – 4.5	4	Polycrystalline by PLD on Pt/Ti/SiO ₂ /Si (100)	D.W. Shin	[29]

Table 3, Electrolytes, solvents, solvent ratios, voltage ranges, C-rates, and cathode build-ups of the graphs shown in figure 4 with their respective references.

Furthermore, $\text{Li}_2\text{Mn}_2\text{O}_4$ stresses cathode material to the point of fractures, due to the Jahn-Teller distortion [9]. Cracking of the particles can lead to a loss of connection to the current collector, further contributing to capacity fade.

Structurally engineered epitaxial thin films might suffer less from the distortions caused by the Jahn-Teller transition due to their limited thickness and single-crystal nature, making it interesting to investigate the overlithiated $\text{Li}_2\text{Mn}_2\text{O}_4$.

4.6 Conclusion

In conclusion, as the current rate increases, the voltage drop of the discharge plateaus is more severe. A linear trend can be used to calculate the internal resistance of the cell. To get the components of this internal resistance one has to resort to methods like Electrochemical Impedance Spectroscopy as shown in chapter 3. There, that technique is employed to hypothesize on why the conductivity of the thin-films is 50 times lower than that for bulk LiMn_2O_4 .

As the current rate increases, the capacity decreases. This is attributed to the high internal resistance causing the voltage plateaus to drop below the cut-off voltage. When including the capacity gained during the 5 min. voltage hold, the difference is much less severe and the voltage hold is therefore nearly enough.

The large resistance to charge-transfer could indicate a high resistance for the Li-ions and/or electrons to reach a suitable intercalation spot, which could be attributed to grain boundaries, or, in the case of high electronic resistance, a problem at the interface between SrRuO_3 and LiMn_2O_4 . Currently, the thin films are capable of high current rates which could further be improved when the large charge-transfer resistance is decreased. SrRuO_3 was already introduced to do so [23], however, the quality of the deposited SrRuO_3 layer could greatly influence the measured resistance. Furthermore, during pulsed laser deposition there is a possibility of intermixing. $\text{Li}_y\text{Ru}_x\text{Mn}_{2-x}\text{O}_3$'s crystal structure is similar to that of Mn_2O_3 and might have therefore been overlooked. Although probably very thin, it might influence the electronic conduction between the thin film LiMn_2O_4 and its substrate. This requires more detailed investigation in future research.

The discharge capacity over cycles shows low degradation over extensive cycling and is comparable to that of bulk LiMn_2O_4 when mostly its $\langle 111 \rangle$ facet is shown. It outperforms polycrystalline thin films found in literature, indicating the importance of interface engineering of the LiMn_2O_4 cathode. Although capacity fade is still present, it is currently attributed to Mn-dissolution even though hardly any interface except the $\langle 111 \rangle$ is in contact with the electrolyte.

4.7 References

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5 Electrochemical response of overlithiated $\text{Li}_2\text{Mn}_2\text{O}_4$ thin film cathode

5.1 Introducing $\text{Li}_2\text{Mn}_2\text{O}_4$

High energy density, power density and longevity are the key requirements of a good battery, as mentioned in chapter 1. Spinel LiMn_2O_4 is a promising cathode material for next generation lithium batteries [1, 2] due to its relatively high operating voltage (4.1 V vs Li) and energy density (theoretically 148 mAh/g, typical 125 mAh/g) combined with low cost and absence of direct environmental or safety hazards. In chapter 2 control over the interface and orientation of the cathode layers was demonstrated allowing good cyclability with longevity over a thousand cycles at a C-rate of 3.3.

The $\lambda\text{-Mn}_2\text{O}_4$ framework can host extra lithium (beyond 1) into empty octahedral (16c) sites, resulting in a 3 V voltage plateau [3]. By discharging the cell below the 3 V plateau, an almost twofold increase in capacity can be achieved as the theoretical specific capacity goes from 148 to 288 mAh/g and the practical specific capacity goes from 125 to 245 mAh/g [4]. Compensating for the added weight of the lithium not 148 but 140 mAh/g is added, resulting in a combined specific capacity of 288 mAh/g. This increases the energy density of the $\lambda\text{-Mn}_2\text{O}_4$ framework to 1027 Wh/kg theoretically, or 873 Wh/kg in practice [4].

The reaction scheme for discharging the $\lambda\text{-Mn}_2\text{O}_4$ framework is shown below in table 1:

Table 1, Reaction scheme for discharging $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode ($0 < x < 2$).

Here the first discharge happens with the two distinct plateaus around 4 V after which another discharge happens around 3 V. The discharge graph is shown in figure 1.

This extra lithium-ion, per unit cell, incorporated at the 3 V plateau, induces a Jahn-Teller distortion in the $\lambda\text{-Mn}_2\text{O}_4$ framework [1,3,5]. The cubic-spinel crystal structure with a lattice parameter of 8.25 Å undergoes a transition to a $9.24 \text{ Å} \cdot (5.65 \text{ Å})^2$ tetragonal spinel structure [1,3,5]. This change in crystal structure, with a 16% increase in the a/c ratio (and 5% in volume), creates large stresses within the material, often cracking it and causing loss of connection to the current collector, which causes loss of capacity [1,3].

Figure 1, Discharge profile for $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode ($0 < x < 2$). Insets show the crystal structure throughout lithiation [3].

Therefore, most studies in literature avoid using the 3 V plateau and limit the discharge voltage to the 4.5 – 3.4 V range [6]. Thin film studies on LiMn_2O_4 that do include it, report a severe capacity fade of 50% within 50 cycles, 4.3 – 2 V range [7] and 15% within 10 cycles, 4.45 – 2.7 V range [8]. However, these are usually not epitaxial thin films as used in this study, but polycrystalline.

In a study by Y.-I. Jang et al. [9] it was shown that by starting with orthorhombic LiMnO_2 the characteristic plateaus at 3 V and 4 V are achieved through consecutive cycling. Orthorhombic LiMnO_2 is stoichiometrically similar to $\text{Li}_2\text{Mn}_2\text{O}_4$ -tetragonal-spinel. Through this process their capacity starts low (40 mAh/g, $\frac{1}{4}$ C, 2 – 4.4 V range) and increases over cycling to 130 mAh/g in 40 cycles after which it stabilizes [9]. While it is debatable if this stability is maintained over longer cycling periods, they propose a suppression of the Jahn-Teller distortion due to cation disorder and the formation of nanodomains. At a rate of $\frac{1}{4}$ C they achieve only 130 mAh/g, however, they are able to achieve almost the theoretical capacity of $\text{Li}_2\text{Mn}_2\text{O}_4$ (270 of 285 mAh/gram) at a low current rate (3.33 mA/g – $\frac{1}{40}$ C).

Even though orthorhombic LiMnO_2 is only able to achieve the high specific capacity at very low currents, it is still very interesting to see the large impact on the total (practical) energy density. Compared to other cathode compounds, mentioned in table 1 of chapter 1, the $\text{Li}_2\text{Mn}_2\text{O}_4$ has the second highest theoretical energy density, and the highest practical energy density. As the formation of nanodomains was proposed to suppress the Jahn-Teller distortion, epitaxial thin films might also exhibit suppressed Jahn-teller distortion. To research this suppression and the impact on the capacity over cycles, the electrochemical response of samples with single {111}-facets and high crystallinity are investigated.

5.2 Experimental results on 100-oriented $\text{Li}_x\text{Mn}_2\text{O}_4$ thin film cathodes

100-Oriented $\text{Li}_x\text{Mn}_2\text{O}_4$ thin films were synthesized following the synthesis route as described in chapter 2. When discharging to voltages below 3 V a charge and discharge peak can be observed in the 3 V plateau region during cyclic voltammetry (indicating $\text{Li}_2\text{Mn}_2\text{O}_4$), and two charge and discharge peaks can be observed in the 4 V plateaus region ($\text{Li}_1\text{Mn}_2\text{O}_4$), see figure 2. Additionally, when discharging to voltages below 3 V, a peak around 3.8 V appears, which does not when discharging till 3 V. The peak at 3.8 V seems irreversible (no direct discharge counterpart), however, remains present during consecutive cycling. It is not

well known where this peak comes from [10], however, an indication for its origin is found in [11] where a sudden volume contraction (possible tetragonal to cubic spinel) occurred. It is hypothesized that Li-Mn defect clusters are formed in which Li is stabilized, therefore requiring a higher voltage to extract this lithium [12]. Similarly to the peak positions in cyclic voltammetry, charge-discharge shows plateaus around the same voltages. Two plateaus can be observed in the 4 V region, one plateau in the 3 V region, and a small plateau at 3.8 V corresponding with the different peaks observed in cyclic voltammetry.

Figure 2, a) Cyclic voltammetry for a thin $\text{Li}_2\text{Mn}_2\text{O}_4$ film at 1 mV/sec. b) Charge - Discharge curve at 1 μA in the voltage range of 4.5 – 2.7 V. At (*) a peak/plateau around 3.8 V is observed which is hypothesized to be Li-Mn defect clusters.

From figure 2 the observed specific capacity for the thin film is much larger (almost 380 mAh/g) than what is theoretically possible (288 mAh/g). Looking at the discharge graph in figure 2b a capacity of about 120 mAh/g for the 4 V plateaus can be observed, as is also achieved in practice. For the 3 V plateau however, the discharge capacity (3.1 – 2.7 V) is over 200 mAh/g, much higher than the theoretically predicted value of 140 mAh/g. On the other hand, the discharge between 3.8 – 3 V shows a capacity of almost 80 mAh/gram as a

certain “tail”. This extra capacity cannot be explained by capacity of the $\text{Li}_2\text{Mn}_2\text{O}_4$ layer alone, as it would require a layer of almost 40 nm thicker ($\sim 1/3$) or a higher lithiation level. A possible explanation is given when the solid electrolyte interphase (SEI) acts as an extra charge reservoir which can significantly contribute to the capacity as was recently suggested by [13].

Moreover, surface effect contributions have been shown to occur for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel causing a similar tail [14 – 16]. As for thin films the surface capacity can have a significant contribution to the electrochemical behavior with respect to the limited volume of the film, it is therefore proposed that this large surface area causes the capacity contribution. The surface is furthermore enhanced for the 100-oriented $\text{Li}_x\text{Mn}_2\text{O}_4$ thin film cathodes as observed as the pyramidal structures in chapter 2.

To minimize the surface contributions, cycling was performed close to either the 4 V plateaus (4.5 – 3.6 V) or the 3 V plateau (3.2 – 2.7 V). The 4V plateaus are cycled for 30 times with a current of 5 μA giving a capacity of almost 120 mAh/g (figure 3a). Subsequent cycling of only the 3 V plateau for 30 times with 1 μA gives a capacity of around 115 mAh/g (figure 3b). These capacities are more in line with the expected practical capacities for $\text{Li}_x\text{Mn}_2\text{O}_4$.

Cycling the 3 V plateau is known to quickly degrade the LiMn_2O_4 cathode material due to the Jahn-Teller distortion [1,3,6-8]. To observe the effect of the distortion or possible suppression, the 3 V region was cycled for epitaxially engineered thin films of $\text{Li}_x\text{Mn}_2\text{O}_4$ in (100)-orientation. The capacity exhibits a rate dependence and indeed cycling the 3 V plateau with 5 μA (figure 4), instead of the 1 μA (figure 3b), reduces the capacity from 116 to 93 mAh/g. During cycling for 300 cycles (figure 4), the capacity is nearly constant.

Figure 3, a) Charge-discharge capacity for the 4 V plateau at $5 \mu\text{A}$ and, b), charge-discharge for the 3 V plateau at $1 \mu\text{A}$. The specific capacities achieved are respectively 119 mAh/g and 116 mAh/g.

Figure 4, Capacity and efficiency over cycles for a thin film of LiMn_2O_4 between a voltage range of 2.7 – 3.2 V at a current of $5 \mu\text{A}$. The capacity is around 94 mAh/gram with an efficiency between 91 – 93%.

Although small variations are visible, these can be attributed to fluctuations in temperature of the lab during the long cycling period.

As discussed, even the best performing LiMn_2O_4 cathodes show a decrease in their capacity over cycling (chapter 4, figure 4). It was previously suggested that increasing the nanodomains in powders through the process of ball-milling for an extensive period of time severely reduces the capacity fade at the 3 V plateau due to strain compensation of the nanograins [17]. As the deformation of particles with smaller grains is less anisotropic, there is less possibility of particle fracture due to the Jahn-Teller distortion. However, it has not been shown before that thin films of $\text{Li}_x\text{Mn}_2\text{O}_4$ can be cycled around the 3 V plateau with negligible loss in capacity.

As the coulombic efficiency of the charge-discharge is between 91 and 93%, not all lithium that has been extracted can be inserted due to parasitic processes such as SEI-layer growth on the surfaces of metallic lithium anode and $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode in the 1M LiPF_6 , 1:1, EC:DMC electrolyte. However, as metallic lithium is present in excess, Li loss due to SEI-layer growth is expected to be negligible in the measurements.

The reversible electrochemical process taking place around 3 V is expected to be the insertion of a Li-ion into LiMn_2O_4 cubic spinel to obtain $\text{Li}_2\text{Mn}_2\text{O}_4$, a tetragonal spinel. The out-of-plane lattice parameter for (001)-oriented thin films should increase from (8.25 Å to 9.24 Å) for the transition of cubic- to tetragonal spinel $\text{Li}_2\text{Mn}_2\text{O}_4$ [12,18]. Therefore, this structural change was studied by XRD (figure 5). Samples were discharged to various voltages and taken out of their cell to observe the out-of-plane lattice parameter change. A pristine sample that has not been cycled nor been in contact with electrolyte is added for comparison.

Figure 5, Out-of-plane XRD intensity over 2θ angle for (100)-oriented thin $\text{Li}_x\text{Mn}_2\text{O}_4$ films. For comparison a thin film before cycling (pristine) is added. Contributions by the Nb:SrTiO₃ substrate (□), SrRuO₃ (*) and impurity (●) are indicated.

All samples show a peak around 38° which is contributed to the impurity phase: Mn_2O_3 . This phase might be present due to lithium deficiency during synthesis at elevated temperatures, as discussed in Chapter 2. Around 46.5° the substrate peaks for Nb:SrTiO₃ and around 46° the SrRuO₃ buffer layer peaks are visible. Between 38.5° till 45.5° peaks can be observed representing various (004)-peaks at different lithiation levels of $\text{Li}_x\text{Mn}_2\text{O}_4$. At a voltage of 4.5 V it is expected that x within $\text{Li}_x\text{Mn}_2\text{O}_4$ is 0 (or $\lambda\text{-Mn}_2\text{O}_4$). Similarly, for 3.1 V, $x = 1$ ($\text{Li}_1\text{Mn}_2\text{O}_4$) and at 2.7 V, $x = 2$ ($\text{Li}_2\text{Mn}_2\text{O}_4$). The peaks for the different voltages and thereby linked lithiation levels in $\text{Li}_x\text{Mn}_2\text{O}_4$ correspond with the lattice parameters found in literature: for $\lambda\text{-Mn}_2\text{O}_4$ the lattice parameter is $8.03 \text{ \AA}$, for $\text{Li}_1\text{Mn}_2\text{O}_4$ (3.1 V) it is $8.25 \text{ \AA}$ and for $\text{Li}_2\text{Mn}_2\text{O}_4$ (2.7 V) it is $9.24 \text{ \AA}$ [12,18 – 20].

This is a strong indication that the cubic to tetragonal-spinel transition takes place without much loss of capacity. With the enhanced energy density of $\text{Li}_2\text{Mn}_2\text{O}_4$ it is very interesting to further research as to why there is minimal capacity fade in epitaxial thin films. It is hypothesized that the stability is partly due to the film thickness and its epitaxial growth. As shown in chapter 4, figure 4, other thin films grown by RF / magnetron sputtering show more severe capacity degradation [21, 22] where, even with a coating [8], a clear degradation is still visible. As the epitaxial growth results in mostly {111}-facets interfacing the electrolyte, the amount of dissolution of Mn is limited as this occurs mostly through the {110} facet [23].

For (100)-oriented $\text{Li}_x\text{Mn}_2\text{O}_4$ films the out-of-plane lattice parameter during the Jahn-Teller distortion goes from 8.25 Å ($x = 1$) to 9.24 Å ($x = 2$) [12, 18 – 20] whereas the in-plane lattice parameter changes from 8.25 Å ($x = 1$) to 5.65 Å ($x = 2$). Due to this, strains caused by the cubic- to tetragonal-spinel transition at the 3 V plateau could cause a reordering of the Mn to take place [24]. During the reordering from tetragonal to monoclinic or orthorhombic transition it was suggested that both result in a structure that is energetically favorable under in-plane stress as opposed to the tetragonal phase. The applied strain leads to redistribution of Mn ions within the oxygen framework. This changes the Mn distribution ratio from 1:3 in alternating layers of the tetragonal phase to a 2:2 distribution in the monoclinic or orthorhombic phase as shown in the figure on the right.

This transition due to the strain could explain the longevity of the cycling at the 3 V plateau. When the strain can be accommodated for by the material, it will not break or lose connection to the current collector, and, therefore, there will be no loss of capacity. X. Chen et al. unfortunately only shows five Cyclic Voltammetry cycles taken at 0.5 mV/sec and no results for extensive cycling [24].

Figure 6, Transition of $\text{Li}_2\text{Mn}_2\text{O}_4$ from tetragonal to monoclinic or orthorhombic due to strain. Adapted from [24].

Upon discharging the 3V plateau, the average Mn-valence state changes from 3.5+ to 3+:

Looking at the dissolution reaction, including the 3 V plateau should increase the Mn^{3+} concentration and therefore increase the Mn-dissolution:

To investigate enhanced dissolution and thereby capacity fade due to including the 3 V plateau, more charge-discharge cycles are done. After an initial 1000 cycles of solely the 4 V plateau (shown in chapters 2 and 4) a cycling period of 300 times at 5 μA between 2.7 – 3.2 V (figure 4) is employed. Thereafter, the 4 V region is cycled again (3.6 – 4.5 V at 5 μA) for 250 times. Even though the capacity does not seem to decrease when the 3 V plateau is cycled, it is clear capacity fade does occur for the 4 V plateaus. Mn-dissolution is therefore not enhanced or even stopped when both manganese reside in the 3+ valence state.

However, the capacity (4.5 – 3.6 V at 5 μA), when cycling the 4V region again *after* a period of cycling the 3 V plateau (3.2 – 2.7 V at 5 μA), has returned to (or slightly above) the capacity (4.5 – 3.6 V at 5 μA) of the very first cycle *before* cycling the 3 V plateau. When

Mn-dissolution is the factor for loss of capacity, the capacity cannot return to its initial value. With dissolution the material goes into the electrolyte causing an irreversible loss of capacity. To elucidate the process behind the possible rejuvenation of the cathode by including the 3 V plateau, the cell was first cycled for 50 times around the 3 V plateau (not shown) after which the cell was further cycled between the 4 V plateaus (4.5 – 3.6 V) and 3 V and 4 V plateaus (4.5 – 2.7 V). In figure 7 (in blue) this is visible as periodically 50 cycles of capacity fade, followed by 10 cycles of both the 3 V and 4 V plateaus.

Figure 7, Capacity over cycles for an epitaxial thin film of LiMn_2O_4 at 3.3 C ($5 \mu\text{A}$).

After 10 cycles of both the 3 V and 4 V plateaus the capacity is apparently rejuvenated and starts to fade again during the 50 cycles at the 4 V plateaus period. This is repeated ten times to observe possible capacity fade of the first cycle after each period of cycling both the 3 V and 4 V plateaus. It is observed that the capacity of the 4 V plateau is continuously brought

back to the initial $\sim 120 \text{ mAh/g}$ capacity when a period of cycling the 3 V plateau was included. No significant decrease in capacity of the first cycle of only the 4 V plateaus is observed. To analyze possible fades and the increases of the 4 V capacity an analysis of the voltage profile is shown in figure 8.

Figure 8, Voltage profile over capacity for an epitaxial thin film of LiMn_2O_4 at 3,3 C ($5 \mu\text{A}$). Inset shows discharge capacity over cycles with A through F denoting different points in the cycling process.

Above, the voltage profile over capacity at different points in the cycling between the two voltage ranges ($10 \times 4.5 - 2.7 \text{ V}$ followed by $50 \times 4.5 - 3.6 \text{ V}$) can be observed. The points in the inset have different discharge over capacity profiles:

- A. Voltage profile after fifty cycles of only the 4 V plateaus (aging).

- B.** Charge after A) and discharge till 3.6 V. A small capacity fade is visible at 3.6 V. The discharge continues down to 2.7 V leading to a high discharge capacity (above 300 mAh/g) as shown in the inset.
- C.** Halfway point of cycling both the 3 V and 4 V plateaus. Discharge capacity at 3.6 V has slightly increased.
- D.** Last point in cycling both the 3 V and 4 V plateaus. Discharge capacity at 3.6 V has further increased. Discharge continues for the last time down to 2.7 V.
- E.** First cycle of only the 4 V plateaus. Discharge capacity at 3.6 V has increased through C, D till E as can be observed from the voltage graph.
- F.** Voltage profile after fifty cycles of only the 4 V plateaus showing capacity fade.

The charge profiles of C and D cannot be observed as they are outside the capacity range as their charging starts at 2.7 V.

5

It is clear that cycling the 4 V plateau leads to the capacity fade that is associated in literature by the Mn dissolution. The shown revival of capacity is only possible if either the structure of LiMn_2O_4 has a reversible Mn-dissolution (i.e. dissolved Mn can reconstruct the $\lambda\text{-Mn}_2\text{O}_4$ framework) or the capacity fade has a different origin. It is hypothesized that one such origin could be insufficient charge and discharge, which accumulates into a fade. However, this would mean an increasing difficulty (voltage fade) in the extraction of lithium which is not observed. One other explanation could be that during charge and discharge at the 4 V plateaus, small amounts of Mn reorganization takes place. The proposed Mn reorganization by X. Chen et al. [24] would then already take place at higher voltages, slowly blocking the pathways for lithium diffusion and therefore decreasing the amount of capacity. As the material is then discharged to 2.7 V the material fully converts and upon charge it changes

back. Doing this several times revives the material, unblocking the lithium pathways and returning the capacity to its original value.

The question then arises if there is any capacity fade at all as the capacity of the 4 V plateau is continuously brought back. As increased temperatures are known to make the Mn-dissolution more severe [25, 26], experiments at elevated temperatures would elucidate if and how severe Mn dissolution takes place in the epitaxial thin films of LiMn_2O_4 .

5.3 Conclusion

Epitaxial thin films with single {111}-facets and high crystallinity are overlithiated from LiMn_2O_4 to $\text{Li}_2\text{Mn}_2\text{O}_4$ by discharging below 3 V. Due to surface effect contributions a large “tail” is visible in the charge-discharge, giving rise to capacities above theoretical values. Contrary to most literature studies on $\text{Li}_x\text{Mn}_2\text{O}_4$, cycling the 3 V plateau did not result in capacity degradation. Out-of-plane structural characterization by XRD shows the lattice parameter of the thin film does change with lithiation, indicating the Jahn-Teller distortion has taken place for $\text{Li}_2\text{Mn}_2\text{O}_4$. Strain compensation is suggested to prevent particle fractures upon Jahn-Teller distortion, therefore, no loss of material and therefore capacity occurs. A structural transition due to in-plane strain could explain the strain compensation of the thin films, where $\text{Li}_2\text{Mn}_2\text{O}_4$ is not tetragonal, but monoclinic or orthorhombic. The Jahn-teller distortion is thus present, but its effect is suppressed to the point where no effect on the capacity over cycles is visible. Furthermore, limited or no Mn-dissolution takes place in the thin films as cycling the 3 V plateaus for 10 cycles is sufficient to rejuvenate the 4 V region capacity to its original value.

This allows for LiMn_2O_4 cathodes which can both 1), cycle deeper to allow the use of 288 mAh/gram instead of the currently only 148 mAh/gram used, and 2), cycle for extensive lifetimes as the capacity is able to be rejuvenated.

5.4 References

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6 Solid-state electrolyte $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ in thin film batteries

6.1 Introducing solid-state electrolyte $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$

Safety is an intrinsic challenge of conventional Li-ion batteries due to the high energy densities and use of flammable liquid electrolytes. While solid electrolytes are expected to exhibit enhanced safety due to higher thermal stability, absence of leakage, and higher resistance to punctures [1 – 3]. Batteries with a solid electrolyte, so-called solid-state batteries, might also be made thinner, as separator, solvents and salts are not needed, which can increase energy density. As compared to liquid electrolytes, however, the solid electrolytes have in general lower ionic conductivities, which is why research is mostly focused on increasing the ionic conductivity [2 – 4]. Furthermore, the solid-solid interface between the electrolyte and anode/cathode becomes rigid, which might cause loss of contact when large differences in temperature expansion coefficients exist or changes in the lattice parameter, during lithiation, occur. As lithium is intercalated into the electrode material, it expands (and contracts again upon de-lithiation), this process can cause loss of contact (over time and cycling) at the interface between the electrode material and the solid electrolyte, increasing the contact resistance [1]. Preferably, an electrolyte can accommodate the changes in the structure of the electrode.

6

Common materials that have been studied to function as solid-state electrolytes are polymers, ceramics and glass materials. A literature overview of state-of-the-art electrolytes is presented in figure 1. $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ perovskite solid state electrolyte is a very promising ceramic electrolyte, showing high ionic conductivities ($\sim 5 \cdot 10^{-4}$ S/cm) around room temperature close to that of a standard liquid electrolyte like 1M LiPF_6 EC:DMC 1:1 (10^{-2} S/cm) [4,5]. It is furthermore a perovskite material with a lattice parameter (3.86 - 3.88 Å [1,6]) close to that of our Nb:SrTiO₃ substrate (3.91 Å). Thereby having a high probability to grow epitaxially on both the crystalline LiMn_2O_4 cathode thin films and Nb:SrTiO₃ substrates.

Figure 1, Overview of state-of-the-art electrolytes showing the ionic conductivity as function of temperature on a Lin-log scale. Adapted from [5]

Therefore, through pulsed laser deposition, $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ is synthesized on Nb:SrTiO_3 substrates with different crystalline surface orientations, and at various synthesis temperatures, to determine the structural and electrochemical dependence of grown thin films on its substrate and synthesis temperature. Afterwards, the solid electrolyte will be combined with a solid anode and the LiMn_2O_4 cathode to determine the structural and electrochemical properties of an all-oxide full solid state battery. Furthermore, creating a nanocomposite could allow for increased contact area, which in turn would allow for an enhanced power density. Therefore, it is tried to synthesize a nanocomposite for solid-state batteries and characterize its structural and electrochemical properties.

6.2 Thin film $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ solid-state electrolyte

The crystal structure of the perovskite $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) is shown in figure 2a. The $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ structure is often described by an orthorhombic structure of two primitive perovskite unit cells stacked on top of each other due to A-site deficiencies in the crystal structure [7,8]. However, when the lithium ratio (x) in $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is high enough ($x > 0.08$), the crystal structure can be regarded as cubic [9, 10].

The stoichiometry of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ has a dramatic effect on the ionic conductivity, as can be seen in figure 2b [11]. For $x = 0.11$ ($\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$) the highest ionic conductivity, due to lithium vacancy controlled diffusion through the LLTO-system, can be achieved along which Li can diffuse [12, 13].

Figure 2, a) Lattice parameter of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ versus lithium ratio, adapted from [9].

Inset of a) shows $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ in spacegroup $P4/mmm$. Black sphere is Ti^{4+} , red spheres are O^{2-} , blue spheres are either La^{3+} , Li^+ or a vacancy. b) Ionic conductivity vs. ratio of lithium in $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ adapted from [14]. Adapted from [15]

To study the influence of the underlying crystal orientation of the substrate on the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin film crystal structure, Nb:SrTiO₃ substrates with (100, 110 or 111)-orientation were used. Synthesis was done through pulsed laser deposition with conditions derived from both the synthesis of LiMn_2O_4 (Chapter 2) and literature [1, 6, 10]. The $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films were grown at various temperatures (700 - 900 °C) on Nb-doped (0.5 wt%) single crystalline SrTiO₃ (100, 110 or 111) substrates from a sintered $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ -target, using a KrF excimer laser operating at 248 nm at a repetition rate of 2 Hz. The Nb:SrTiO₃ substrates were annealed at 950 °C for 1.5 h in an oxygen flow of 150 ml/min. The oxygen pressure during growth was 0.2 mbar (20 Pa), while the laser energy fluence was 2.3 J cm⁻². After deposition, the thin films were cooled down to room temperature in an oxygen pressure of 1 bar at a rate of 10 °C min⁻¹ to optimize the oxidation level.

X-ray diffraction was used to study the epitaxial relation between the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films and the Nb:SrTiO₃ substrates. Firstly, the temperature was varied to observe the lowest point at which good crystallinity can be observed, to minimize the lithium deficiency due to evaporation. In figure 3a clear peaks of the Nb:STO (100) substrate as well as peaks of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, marked with their respective orientation, can be observed. Although $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is clearly present for the higher temperatures, a significant contribution of anatase and rutile TiO_x phases are still observed. Additionally, more rutile phase peaks would be expected as they are favored over anatase at these high temperatures [16], however a large anatase contribution is still present.

The rutile and anatase phases indicate lithium deficiencies, similar to the formation of Mn_2O_3 impurities as observed in the synthesis of LiMn_2O_4 shown in Chapter 2.

Figure 3, Out-of-plane XRD intensity over 2θ angle for $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films grown on Nb:STO-100 at various temperatures (700 – 900 °C). b) is a zoom-in between 45 – 48 degrees in 2θ of a). Contributions by the Nb:SrTiO₃ substrate (□) and impurities anatase TiO_x (A) and rutile TiO_x (R) are indicated.

In figure 3b a strong intensity for the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (200)-peak at 800 and 900 °C can be observed, indicating epitaxial thin film growth.

From 3b, the (200)-peak position is determined by subtraction of the Nb:SrTiO₃ peak from a bare substrate XRD (not shown). This gives, for 800 and 900 °C, a peak position of 46.9° with a corresponding lattice parameter of 3.872 Å. Using figure 2a, the lattice parameter is used to estimate the lithium concentration to be close to $x = 0.13$ for the 800 and 900 °C samples. As for the 700 °C synthesis the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ peak is hardly visible, this indicates that this temperature is insufficient to synthesize crystalline $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$. To minimize the lithium deficiency due to evaporation of lithium at high temperatures, the lowest temperature (800 °C) at which crystalline $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is formed is used for follow-up synthesis.

The topography for $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films grown on the three different orientations of Nb:STO ((100), (110) & (111)) is shown in figure 4. Clear cubic / rectangular features are visible in the AFM images of the (100) and (110)-oriented $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films in the vertical and horizontal direction, indicating an in-plane relation to the Nb:SrTiO₃ substrate, while in the (111) orientation no clear shape can be distinguished. Roughness (RMS) values are 5.61, 1.38 and 2.03 nm for respectively the (100), (110) and (111)-oriented films which have a thickness of about 100 nm as determined through cross-section SEM (not shown).

In figure 5, XRD is shown of the same samples. Substrate peaks are marked as well as the peaks of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ with their respective orientations. The out-of-plane XRD gives a hint for an epitaxial relation between substrate and thin-film which in-plane XRD could prove. Due to the similarity of the growth to that of LiMn_2O_4 it is assumed to be epitaxial. All $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films show contributions of the rutile and anatase TiO_x phases.

The cubic / rectangular features in the AFM images are attributed to the anatase TiO_x -phase as the perovskite $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is expected to grow coherent flat layers on the perovskite Nb:STO substrate due to energetically favored facets [17, 18].

Figure 4, AFM topography of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films on Nb:STO-((100), (110) & (111)) at 800 °C. Inset shows height profile over the (100)-oriented surface.

Figure 5, a) Out-of-plane XRD intensity over 2θ angle for $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films grown on ((100), (110) & (111))-Nb:STO at 800 °C. b) is a zoom-in of the main substrate peak with the main $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ peak. Contributions by the Nb:SrTiO₃ substrate ($\square$) and impurities anatase TiO_x (A) and rutile TiO_x (R) are indicated

6.3 All-oxide full solid state batteries

Through a study on synthesizing epitaxial thin films of the anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [19] it becomes possible to synthesize the three key elements of the battery: Anode ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), Electrolyte ($\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$) and Cathode (LiMn_2O_4). As mentioned in the introduction of this chapter, the advantages of a solid electrolyte are mainly enhanced safety and increased energy density with the disadvantage of low Li-ion diffusivity and difficulties in coating and maintaining interfacial connection. On the other hand, a reduced thickness of solid electrolyte could still allow for sufficient lithium diffusion. In Chapter 3 the Li-diffusivity through LiMn_2O_4 was measured to be roughly around $4 \cdot 10^{-14} \text{ cm}^2\text{s}^{-1}$ whereas that of the electrolyte is reported to be higher than $10^{-11} \text{ cm}^2\text{s}^{-1}$ [20]. A limited Li-conducting $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ electrolyte does not have to be the bottleneck for a full solid-state battery,

this might actually be the diffusivity through the cathode / anode. To synthesize a full stack of the materials, some crucial limitations have to be taken into account. The deposition temperature of LiMn_2O_4 is limited to about 600 °C as higher temperatures result in a structural change that is no longer electrochemically active as shown in chapter 2. Furthermore, LiMn_2O_4 can have interfacial reactions at higher temperatures [1]. As both the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ need higher synthesis temperatures of respectively 700 and 800 °C they have to be synthesized before LiMn_2O_4 . However, as the electrolyte ($\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$) needs to be synthesized in between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiMn_2O_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ needs to exceed its synthesis temperature. Luckily, in the study on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ no structural change was observed at elevated temperatures (>800 °C) after synthesis at 700 °C. Therefore, the build-up of the all-oxide full solid-state battery will start with a layer of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ followed by $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ and lastly LiMn_2O_4 : “Nb:SrTiO₃ / $\text{Li}_4\text{Ti}_5\text{O}_{12}$ / $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ / $\text{Li}_x\text{Mn}_2\text{O}_4$ ”.

The anode material ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) has a voltage of 1.5 V vs. Li and the cathode material (LiMn_2O_4) a voltage of 4 V vs. Li, therefore a potential difference of 2.5 V is expected. On the one hand the energy density is increased by using solid state materials, while on the other it is decreased due to the choice of materials, which is one of the reasons to research high potential cathodes [21]. Despite this, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is chosen, as lithium metal is very reactive, many electrolytes decompose at low voltages vs. Li [22, 24]. An $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode provides a higher voltage and is thus not as reactive. The $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, does not react with this anode, whereas vs. lithium metal it would undergo lithium insertion and decompose. Although, Y. Zhu et al.[23] showed that the decomposition energy for $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is very low, preventing the decomposition from occurring quickly, it could still quickly decompose the thin film.

The voltage vs. Li of the LiMn_2O_4 cathode potential during cycling can rise above 4.5 V. The stability of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ at high voltages (versus LiMn_2O_4) can become unsure [22, 24]. However, it has been shown that amorphous $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ can be stable (no lithium extraction occurs) up to 12 V with blocking electrodes [4]. Furthermore, $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ has been shown in a previous study to work in combination with LiMn_2O_4 [1].

With a thinner electrolyte a higher energy density can be achieved, the electrolyte only has to prevent a short between cathode and anode (i.e. coat the thin layer) as well as show a sufficient Li-diffusivity. The thickness for LiMn_2O_4 is around $\sim 100\text{nm}$ as shown in previous experiments (Chapter 2) and through the study on synthesizing epitaxial thin films of the anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [19] the thickness of this anode is matched. The matching is used in order to intercalate the same amount of lithium ions that is extracted from the LiMn_2O_4 layer upon charge and vice versa upon discharge. This resulted in the all-oxide full solid state stacks shown in figure 6:

Figure 6, SEM images of All-Oxide Full Solid State Battery on (100)- (left) and (111)- (right) oriented substrate consisting of the anode $\text{Li}_4\text{Ti}_5\text{O}_{12}$, solid-state electrolyte $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ and cathode LiMn_2O_4 .

In the SEM images, the secondary electron detector image (standard) is combined with the Energy Selective Backscattering (ESB) detector image, which shows contrast based on density / atomic mass differences of the materials. As the Lanthanum in the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ layer is a heavy element (similar to the Strontium in the SrTiO_3 substrate) it results in a layer showing up brighter. For the (100)-oriented substrate, the first layer ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) has a high surface area, as is common for spinel material on (100)-perovskite substrates due to the energetically favored facets of the spinel material grown on the perovskite substrate [18]. This might result in the large grains observed in the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ layer grown on top of it. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ layer grown on the (111)-oriented substrates shows much lower surface roughness, as expected for a spinel material grown on a (111)-oriented perovskite substrate [18]. Furthermore, due to the energetically favored facet of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -spinel material, consecutive layers can also have lower surface roughness. In the (100)-oriented stack of layers, a darker rod-like feature through the electrolyte layer can be observed. As it is darker than the anode or cathode layer in the ESB images, it is expected to be composed of light elements (such as Li. metal) connecting the cathode and anode. This could cause shorts between the anode and cathode, preventing electrochemical cycling of the full stack.

To structurally characterize the different layers, XRD is used. Again, clear peaks are visible from the substrate, together with the LiMn_2O_4 peaks, $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ peaks and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ peaks. All three deposited layers take the orientation of the substrate and grow oriented in the same direction (figure 7).

Figure 7, XRD of All-Oxide Full Solid State Battery on (100)- and (111)-oriented Nb:SrTiO_3 substrate consisting of the anode $\text{Li}_4\text{Ti}_5\text{O}_{12}$, solid-state electrolyte $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ and cathode LiMn_2O_4 marked in their respective color. Contributions by the Nb:SrTiO_3 substrate ($\square$) and impurities anatase TiO_x (A) and rutile TiO_x (R) are indicated.

6

Taking the peak-position of (400)- $\text{Li}_x\text{Mn}_2\text{O}_4$ to be 43.84° , results in a lattice parameter of about $8.26 \text{ \AA}$, and therefore, based on [24], a lithium concentration estimated to be around 0. Based on our own measurements in chapter 5 (figure 5) the lithium concentration would be estimated to be 1 ($x=1$, $\text{Li}_x\text{Mn}_2\text{O}_4$) as the peak-position corresponds best to that of the pristine or 3.1 V (400)-orientation peak. This difference between bulk and thin film could be explained by strain from the substrate. Therefore, as the $\text{Li}_x\text{Mn}_2\text{O}_4$ layer is the third of three relative thick layers, any strain induced by the substrate or through the layers below is

expected to be negligible. The peak position, and thereby lithium concentration, is therefore more likely to coincide with that of bulk and thus 0.

Comparing the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ peak intensity here to that after synthesis on a Nb:SrTiO₃ substrate as shown in figure 3 & 4, the intensity has clearly dropped. From this it could be concluded that the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -layer is less crystalline than expected and therefore only a small shoulder with low intensity is visible next to the peaks of the (100)- and (111)-oriented substrates. However, as the next layer ($\text{Li}_x\text{Mn}_2\text{O}_4$) grown on top shows clear epitaxial crystallinity, it is more likely that a decrease in lithium concentration led to an increase in c-axis parameter as shown in figure 2a where the lattice parameter of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ versus lithium ratio is shown from [9]. A common suggestion would be to synthesize at a lower temperature so less lithium evaporation would take place. However, as seen in figure 3, this would reduce crystallinity. A higher pulse frequency of the PLD-laser would allow for less evaporation time for the lithium, possibly increasing its concentration, although faster deposition might also result in lower crystallinity. It is suggested to research this in a follow up study.

Additional peaks around 37° and 80° on the (100)-oriented substrate are observed, which are characterized as a $\text{Li}_1\text{Ti}_1\text{O}_2$ phase. As the peaks of the $\text{Li}_1\text{Ti}_1\text{O}_2$ -phase are very strong it is expected that a large portion of the $\text{Li}_1\text{Ti}_1\text{O}_2$ -phase is synthesized at the cost of the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -phase. However, looking at the stoichiometry of the target materials the Lanthanum must remain somewhere, but does not show up by XRD characterization.

Part of the presence of the $\text{Li}_1\text{Ti}_1\text{O}_2$ -phase in the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -layer could be due to a change in its underlying layer. The template on which thin film growth will happen has changed as $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is grown on top of the synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$, instead of the

Nb:SrTiO₃ substrate. The anode material Li₁Ti₁O₂ is a good electronic but poor ionic conductor [25] and, therefore, severely hampers the effectiveness of the electrolyte layer.

Further investigation and synthesis optimizations to reduce the amount of this Li₁Ti₁O₂ phase is critical. Reduction of the TiO_x-phases is advised as they can be lithiated to Li₁Ti₁O₂ at low voltages of around 1.5 V [26].

While electrochemically characterizing the layers, clear resistance behavior is shown by an open-circuit-voltage of around 0 V and a current linearly increasing with the applied voltage. As the synthesized layers are extremely thin while the electrolyte is expected to be electronically isolating, a dark rod as seen in figure 6 (*) could lead to shorts. Furthermore, edge effects on the substrate can no longer be neglected. During synthesis also some deposition takes place on the edges of the substrate, when sufficiently thin, these can cause shorts as well. Also, due to off-stoichiometry of the electrolyte layer it might have high electronic conductivity. For Li_{3x}La_{2/3-x}TiO₃ it is observed it can become highly electronic conducting when too much lithium is inserted [2]. However, as synthesis is done through PLD, and lithium is very volatile, this higher amount of lithium compared to the target composition is very unlikely. It is more likely that the thin electrolyte layer suffers from shorts as well as edge effects that cause additional shorts. As the (111)-oriented layers showed no shorts, this sample had a part cut out from its middle with a diamond pen. This way, edges (with shorts) which developed during synthesis can no longer contribute and conduction along the edges can be dismissed. This improved the total resistivity of the layer, however subsequent cyclic voltammetry measurements still did not show battery behavior. Instead, its resistance around 0 V was still low with diode like behavior as the current sharply increases above 2 V.

Further research and optimization of the synthesis conditions is required to further investigate this all-oxide full solid state battery. The focus of future research is advised to be on both the interface between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, as well as optimizing the growth conditions of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ on $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

6.4 Nanocomposites of LiMn_2O_4 and $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$

The ability to synthesize a 3D structured battery allows enhanced surface area, as well as more control over this surface area, which enables the exploration of batteries with increased power densities. As the schematic in figure 8 shows, a 2D thick film allows for high specific energy densities due to high loading (high percentage of active material in the anode/cathode part) and relatively large thickness of the anode/cathode. A 2D thin film allows for relatively high power densities by using lower levels of loading (relatively lower amount of active material) and a relatively thin thickness enabling fast lithium transport to the electrolyte. A 3D structure allows use of both advantages, as it combines the large lithium loading with fast lithium transport.

As mentioned in chapter 5, volume expansion of the active anode/cathode material can cause cracking of the material, losing connection to the current collector [27, 28]. When the electrolyte is no longer a liquid but a solid, also loss of connection to the electrolyte can occur, causing an increasing interface resistance over cycling. When an epitaxial film is grown layer-by-layer, on a single crystalline substrate allowing alignment of the crystal orientations, reductions in the resistance to ionic diffusion within both the solid electrolyte and the electrode/solid electrolyte interface can be expected [1].

When a 3D architecture is used, the surface is further increased and the diffusion distance from within the electrode to and from the electrolyte is decreased allowing for faster lithium-

ion exchange. Furthermore, thicker electrode layers are allowed without significant increase in internal resistance as now the electronic transport becomes limiting, which is much faster than the ionic transport [28]. This also allows for higher loadings, both of which contribute to an increase in both specific power and energy density [28] (figure 8).

Figure 8, Schematic of battery architectures for high specific energy density (2D thick film), high specific power density (2D thin film), and both high specific power and energy density through 3D architecture.

Previous studies on nanocomposites by H. Zheng et al. suggest that the combination of a perovskite material with a spinel material will result in phase separation of the two materials during PLD growth [17, 18]. This phase separation, combined with alignment of the nanocomposite, results in so-called Vertically Aligned Nanocomposites (VANs).

Although various epitaxial VANs have been studied in the last decade [29, 30], no lithium-based VANs have yet been explored for energy storage. Realization of two-phase epitaxial VANs has been limited to specific material combinations such as ferroelectrics (BaTiO_3 ,

BiFeO_3 , PbTiO_3) with ferromagnets (CoFe_2O_4 , NiFe_2O_4 , MgFe_2O_4). Within these systems, studies on the ionic conductivity have been limited to that of oxygen ions for solid oxide fuel cells [31] and not lithium. Understanding diffusion of lithium ions in an epitaxial VAN during intercalation, across an epitaxial interface between an electrode and an electrolyte in a solid-state battery, is crucial but has so far remained unexplored.

Several growth mechanisms for the formation of epitaxial two-phase nanocomposites have been proposed in previous studies that lead to different morphologies, such as nanopillars in a matrix, two-phase domain structures, and nanocheckerboard structures [32]. Thermodynamics and kinetics during the thin film growth are the two major factors for the final film morphology, although the exact influence of these two parameters on the overall nanocomposite structure remains complicated to model [30]. In the publications of H. Zheng et al. nanocomposite self-assembly was demonstrated for magnetic and ferroelectric materials, allowing the ability to synthesize a 3D material during PLD [17, 18]. Furthermore, thermodynamics and kinetics can easily be influenced during PLD through parameters as substrate temperature, (oxygen) background pressure, target composition and laser fluence.

This allows creation of a material with a 3D architecture exhibiting extremely high surface area with respect to the cathode and/or anode through self-assembly. Previous research has focused mainly on achieving a 3D architecture through, for example, (cleanroom) selective etching of substrates [28]. Where the 3D architecture might exhibit high surface area and thus allow for high power density, depositing the 3D architecture on a large bulk of the active material (cathode / anode) might not only increase the specific power density, but also the specific energy density of the cell relative to a flat 2D film.

H. Zheng et al. explains this self-assembly through the differences in diffusion energy of the materials with respect to the substrate, much like the nucleation and growth mechanism

described in [32]. During growth, the species at the film surface phase-separate into the nanostructure, which is then part of the bulk film. They demonstrate this by means of the cubic spinel CoFe_2O_4 and perovskite BiFeO_3 . The CoFe_2O_4 material (CFO) is a cubic spinel oxide with a lowest energy surface of $\{111\}$. During growth on a (001)- SrTiO_3 substrate the CFO only partially wets the substrate and forms islands with $\{111\}$ facets. In figure 9 A1 this can be seen as the tip of the octahedron passing through the (001)-oriented substrate surface. BiFeO_3 (BFO) is a perovskite that completely wets a (001)-oriented SrTiO_3 substrate and grows layer-by-layer, shown in figure 9 A1 as a flat surface on top of the (001) oriented substrate.

Figure 9, Schematic representation of CoFe_2O_4 -spinel (dark grey) and BiFeO_3 -perovskite (light grey) growing on a perovskite substrate in a) (100)-, b) (111)-, and c) (110)-orientation. d-f) SEM images of the grown nanocomposites. a-f) adapted from [21].

Due to the surface energies, for a (111)-oriented SrTiO_3 substrate (figure 9 b), this results in complete wetting of the substrate by the cubic spinel CFO while the BFO perovskite will only partially wet the substrate and cause pyramidal nanostructures / nanopillars to grow inside the CFO matrix. As for the (110)-oriented substrate, the difference between the surface energies is less clear, phase separation occurs due to the immiscibility of the materials but a clear matrix / nanopillar composite cannot be shown.

Figure 10, Crystal structures of, a), $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -perovskite and, b), LiMn_2O_4 -spinel.

$\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is a perovskite (figure 10a) that can be grown in very flat layers during deposition on a perovskite substrate, while LiMn_2O_4 is a cubic spinel (figure 10b) that during growth on the (001) oriented substrate forms islands with $\{111\}$ facets (chapter 2).

Therefore, when CoFe_2O_4 is substituted for LiMn_2O_4 and BiFeO_3 for $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, a nanocomposite is obtained of the used cathode and electrolyte material with a 3D architecture achieved through self-assembly. Due to the epitaxial nature of the materials LiMn_2O_4 and $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ on Nb:SrTiO_3 substrates, it allows further control over the interfaces, size, and composition of the nanocomposites. On top of that, the PLD parameters allow further control over the thermodynamics and kinetics during growth.

The $\text{LiMn}_2\text{O}_4 - \text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ thin films were grown by pulsed laser deposition (PLD) at a temperature of 750 °C on Nb-doped (0.5 wt%) single crystalline SrTiO_3 (100, 110 or 111) substrates from sintered $\text{LiMn}_2\text{O}_4 - \text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (1:2), using a KrF excimer laser operating at 248 nm at a repetition rate of 2 Hz. The Nb- SrTiO_3 substrates were annealed at 950 °C for 1.5 h in an oxygen flow of 150 ml/min. The oxygen pressure during growth was 0.2 mbar (20 Pa), while the laser energy fluence was 2.3 J cm^{-2} . After deposition, the thin films were cooled down to room temperature in an oxygen pressure of 1 bar at a rate of 10 °C min^{-1} .

Figure 11, Crystal structures of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -perovskite (blue) and LiMn_2O_4 -spinel (red) nanocomposites grown on Nb: SrTiO_3 -perovskite in orientations (100), (110) and (111). Contributions by the Nb: SrTiO_3 substrate ($\square$) and impurities Mn_2O_3 ($\bullet$), anatase TiO_x (A) and rutile TiO_x (R) are indicated.

XRD characterization indicates that both the LiMn_2O_4 and $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ phases are stabilized within the nanocomposite thin film and epitaxially aligned to the substrate orientation (figure 11). This indicates that the self-assembly that takes place for the

nanocomposite $\text{CoFe}_2\text{O}_4 - \text{BiFeO}_3$ also takes place for the $\text{LiMn}_2\text{O}_4 - \text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ combination. Interestingly, the self-assembly seems to stabilize the LiMn_2O_4 at high temperatures, normally not achievable (chapter 2). Epitaxial strain from the perovskite matrix could have induced the formation of spinel nanopillars. As far as the author knows this is the first observation of a lithium-based epitaxial VAN and allows the construction of 3D battery architecture as proposed and shown in figure 8.

Various additional peaks are observed for the (100)-oriented substrate that correspond to the inhomogeneities as observed in figure 4. These are linked to TiO_x -phases and Mn_2O_3 which could indicate that the stoichiometry of both $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ and LiMn_2O_4 cannot be maintained during deposition and impurities occur due to lithium deficiency.

Using SEM to image the synthesized material (figure 12), surfaces similar to previous studies on non-lithium nanocomposites are visible [17, 18]. For the (100)-oriented substrate rectangular domains are visible on the surface, while for the (111)-orientation triangular domains are visible similar to those shown in figure 9. For the (110)-oriented substrate, however, the surface looks like a matrix of one material, with another material growing elongated domains with have a rooftop-like surface. It is expected that the matrix of these nanocomposites is formed by the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ and perovskite on perovskite growth occurs with the LiMn_2O_4 -spinel forming the columns inside this matrix.

Figure 12, SEM image of the nanocomposites grown by simultaneous deposition of LiMn_2O_4 -spinel and $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -perovskite on perovskite Nb:SrTiO_3 at 750 °C. Bottom images show cross-section views by the Energy Selective Backscatter detector.

By using an Energy Selective Backscatter (ESB) detector, as opposed to the normal secondary electron detector, contrast based on atomic weight and therefore composition can be obtained. For the $\text{LiMn}_2\text{O}_4 - \text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ nanocomposite, the atomic weight difference between Mn and Ti is low compared to La, most contrast is therefore expected from the difference between Mn and La. Looking at the cross-sections in figure 12, good contrast can be seen between the columns and the matrix. Furthermore, contrast between LiMn_2O_4 and the Nb:SrTiO_3 substrate is clear due to the heavy Sr inside the substrate. As there is clear contrast between the columns and the substrate, it can be concluded that the columns are of the LiMn_2O_4 -spinel material while the host is the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -perovskite grown on the perovskite Nb:SrTiO_3 substrate for the orientations (100), (110) and (111). This suggests a battery material with 3D architecture through self-assembly can be realized.

To characterize the electrochemical behavior of the battery material Charge – Discharge and Cyclic Voltammetry measurements are performed. Cyclic Voltammetry is performed at 1 mV/sec between 4.8 V and 3.3 V. During Charge – Discharge a current of 5 μA is used to

charge to 4.6 V and discharge to 3 V. This allows to characterize the electrochemical behavior expected to occur around the 4 V plateaus of LiMn_2O_4 .

Samples are assembled as mentioned in Chapter 2's Cell assembly, where the substrate functions as current collector for the thin film cathode material. A separator soaked with 600 μL , 1M LiPF_6 in EC:DMC 1:1, electrolyte is inserted to prevent the protruding LiMn_2O_4 columns from the nanocomposite to contact the Li metal anode. Performed charge – discharge cycles are shown in figure 13. Specific capacity for the LiMn_2O_4 cathode material inside the nanocomposite ($\text{mAh/g}_{\text{LMO}}$) is estimated based on the ratio between the two materials ($\text{LiMn}_2\text{O}_4 - \text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (1:2)) and a layer thickness estimated by cross-section SEM to be around a 100 nm.

Figure 13, a) Charge – Discharge cycles, and, b), Cyclic Voltammetry of the $\text{LiMn}_2\text{O}_4 - \text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ nanocomposite. The first cycle (1) is indicated, as well as the direction and height of the peaks (arrows) upon consecutive cycling.

In figure 13 the characteristic peaks and plateaus for LiMn_2O_4 are not clearly visible. During cyclic voltammetry a semi-reversible redox reaction is taking place around 3.6 V. Furthermore, during the charge – discharge, there is a large specific capacity of over 200 $\text{mAh/g}_{\text{LMO}}$ of the layer when discharging between 4.6 and 3.0 V which is much larger than

the theoretical $148\text{mAh/g}_{\text{LMO}}$ that could be expected in this voltage range. As deposition is done at elevated temperatures ($750\text{ }^\circ\text{C}$), allowing to achieve the phase separation needed to obtain self-assembly, it might be possible for Ti to replace Mn in the LiMn_2O_4 -spinel leading to the structurally similar $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ [33]. These higher temperatures might explain the intermixing of Ti into the LiMn_2O_4 which is later confirmed by TEM electron energy loss spectroscopy (EELS) (figure 14). From the LiMn_2O_4 depositions (chapter 2) it is known that $600\text{ }^\circ\text{C}$ is the optimal synthesis condition and from literature it is known that LiMn_2O_4 undergoes interfacial reactions at higher temperatures [1].

As the amount of cathode material could be enriched due to Ti insertion, this could contribute to a higher capacity compared to the capacity estimated from Mn alone [33]. However, the capacity is much larger than anticipated and possible intermixing of Ti into the LiMn_2O_4 -spinel would not contribute to a voltage plateau or voltage peaks at 3.6 V .

To further investigate the intermixing and the interface between SrRuO_3 and LiMn_2O_4 , TEM combined with EELS is used (figure 14). Energy loss analysis by TEM-EELS shows a Ti signal throughout the spectrum image. As oxygen shows negligible change and manganese shows a clear drop while lanthanum steeply increases during $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, it is concluded that Ti has indeed intermixed with LiMn_2O_4 -spinel to form $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$.

Figure 15 shows TEM along the (110) direction of LiMn_2O_4 . Clear positions for the different atoms of LiMn_2O_4 are visible and made clear through the inset in 15a. As a guide the crystal structure of LiMn_2O_4 is added in 15b showing both the full crystal unit cell as well as viewed along the (110)-direction. From figure 15c it became apparent that a $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ layer of a few unit cells thick resides between the current collector layer and $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ cathode crystal.

Figure 14, TEM electron energy loss spectroscopy on the nanocomposite of LiMn_2O_4 -spinel and $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -perovskite on $\text{Nb}:\text{SrTiO}_3$ -perovskite substrate. a) Energy loss intensity over the line drawn in c) going from a LiMn_2O_4 column (1) through the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ matrix (2) towards another LiMn_2O_4 column (3). Corresponding element energy losses are indicated. b) Normalized intensity of the elements of a) showing composition change over the line drawn in c).

Figure 15, a) TEM along the (110)-direction of LiMn_2O_4 . b) Crystal structure of LiMn_2O_4 and along the (110)-direction. c) Cross-section TEM of (100)-oriented nanocomposite showing $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ under $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ and covering the SrRuO_3 current collector.

From Suzuki et al. [34, 35] it is known that the interface between the LiMn_2O_4 and the current collector is crucial to a good performance of the LiMn_2O_4 cathode. This could explain the absence of LiMn_2O_4 plateaus; since $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ should be an electronic isolator, the $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ might be fully isolated from the current collector and, therefore, does not participate in the electrochemistry.

To exclude external contributions, electrochemical measurements on a bare substrate are performed where the substrate functions as current collector and “cathode” material. A separator soaked with 600 μL , 1M LiPF_6 in EC:DMC 1:1, electrolyte is inserted to prevent the substrate from contacting the Li metal anode. Performed charge – discharge cycles are shown in figure 16.

Figure 16, Charge – Discharge of the nanocomposite thin film compared to that of a Nb:SrTiO_3 substrate without thin films. Difference in discharge capacity is shown separately.

During charge – discharge (figure 16) it can be observed that external contributions add to the measured capacity. However, these do not explain the small plateau around 3.6 V as visible through the capacity difference graph.

As TEM shows there is Ti present in the Mn-spinel, it is concluded that, even though phase-separation takes place, intermixing also occurs. This hinders the formation of ‘pure’ LiMn_2O_4 and instead presents a structurally, almost identical material: $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$. This material has a lower potential and does not have a clear plateau in the measured voltage region [19, 36].

As $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ does not suffer from Jahn-Teller distortion and can have high capacities (up to 290 mAh/g) it is an interesting material [36]. Furthermore, it is surrounded by electrolyte, allowing for high-speed electrochemistry, allowing the high specific power and energy densities which are the aim of this nanocomposite. However, a high internal resistance seems to hinder good electrochemical performance. The $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ layer beneath the $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ has to be removed to avoid the high resistivity currently observed. It is advised to modify the template on which the nanocomposite is grown, either by surface modification of the Nb:SrTiO₃ substrate or by growing a thin layer of the cathode LiMn_2O_4 before the nanocomposite. This will prevent growth of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ underneath the cathode and will allow high-speed electrochemistry.

6.5 Conclusions

The solid state electrolyte $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ showed the best structural crystallinity when synthesis was done at 800 °C, with a stoichiometry estimated to be $x = 0.13$. For synthesis at 700 °C clear crystalline peaks remained absent. Synthesis on oriented Nb:SrTiO₃ substrates ((100), (110) & (111)) results in thin films with identical orientation, all of which contain TiO_x phases as impurity. These TiO_x phases are most likely due to lithium

deficiencies similar to the Mn_2O_3 impurities observed in Chapter 2. As $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is expected to grow relative flat layers, the observed cubic / rectangular domains on the surface are attributed to the TiO_x phases.

Due to temperature restriction of LiMn_2O_4 to 600 °C, stacks of all-oxide full solid-state batteries were synthesized by starting with the anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$, followed by the solid electrolyte $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, and finalized by the cathode LiMn_2O_4 , where the thickness of the anode is matched to intercalate the same amount of lithium ions as the cathode. XRD shows all three deposited layers take the orientation of the substrate. $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ is less crystalline due to lithium loss and growth on top of the anode, instead of the Nb:SrTiO_3 substrate, causing $\text{Li}_1\text{Ti}_1\text{O}_2$ formation at the cost of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$. This $\text{Li}_1\text{Ti}_1\text{O}_2$ could also cause shorts and thereby the ohmic behavior observed in electrochemical analysis. Further research and electrochemical characterization of the all-oxide full solid-state battery requires the quality of the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ electrolyte layer to be improved.

A 3D architecture nanocomposite was made by synthesis of LiMn_2O_4 -cathode simultaneously with $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -electrolyte. This is a first lithium based vertically aligned nanocomposite for energy storage application. As observed by SEM and confirmed by XRD, a self-assembled vertically aligned nanocomposite was formed aligned to the Nb:SrTiO_3 substrate with increased surface area between the two materials. XRD, furthermore, shows that again the materials take the orientation of the substrate.

Upon charge – discharge cycling and cycling voltammetry, the characteristic peaks of LiMn_2O_4 cannot be found. Instead, a plateau / semi-reversible redox peak is observed around 3.6 V. TEM-EELS confirms the intermixing of Ti into LiMn_2O_4 giving rise to $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ in accordance to interfacial reactions shown in literature to occur at the elevated temperatures used to synthesize the nanocomposite. Furthermore, large internal resistances

found during charge – discharge cycling are explained by TEM showing a few unit cells of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -electrolyte underneath the $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ cathode, hindering the cathode from connecting to the current collector.

A large contribution in the measured capacity of the nanocomposite is from the substrate. However, when the substrate contribution is subtracted, an unexplained plateau around 3.6 V remains which cannot be attributed to the formed $\text{LiMn}_{2-x}\text{Ti}_x\text{O}_4$ -phase.

When the template on which the nanocomposite is grown is modified, either by surface modification of the $\text{Nb}:\text{SrTiO}_3$ substrate or by growing a thin layer of the cathode LiMn_2O_4 before the nanocomposite, it will possibly prevent growth of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -electrolyte underneath the cathode and will allow high-speed electrochemistry. When this is further combined with the ability to also cycle the 3 V plateau of LiMn_2O_4 as shown in chapter 5 it will allow for model epitaxial ceramic battery systems with both higher energy and power density.

6.6 References

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7 Summary

Since their introduction in the 1990's lithium ion (Li-ion) batteries have become the main power source for many portable and stationary applications due to their high energy and power densities. Despite this, research is still ongoing to further enhance these properties of the batteries, as well as making them safer and more environmentally friendly.

Three major intercalation cathode materials (the olivine LiFePO_4 , the layered LiCoO_2 and the spinel LiMn_2O_4) are identified. Their different lithium diffusion pathways influence the cycle-life and lifetime of the used cathode. Their interphase with the electrolyte, and stability thereof, influences the safety of the battery. LiMn_2O_4 cathode material is known as a promising cathode material due to its 3D lithium pathways for diffusion and ability to intercalate a second lithium ion at 3 V. However, literature has shown that it suffers from capacity fade and poor cycle performance due to Mn-dissolution and a Jahn-teller distortion. Although various strategies have been suggested to minimize or prevent these limitations, a model system to study the lithiation mechanisms in detail is needed.

Therefore, highly controlled thin films are made to provide an excellent model system to study these mechanisms as well as to elucidate the possible limiting factors, including Li-ion diffusion, Li-ion transport, and electronic transport. By applying epitaxial engineering where thin films are grown on different oriented Nb:SrTiO_3 substrates, the crystal orientation of LiMn_2O_4 is controlled. This enables a unique insight into the relation between electrochemistry, interface and crystal directionality, not obtainable in single crystals or polycrystalline samples, and previously poorly obtainable in epitaxial films. High discharging rates with good energy capacity and good cyclability is achieved, demonstrating

enhanced cycle life without excessive capacity fading as compared to previous polycrystalline studies.

By using Electrochemical Impedance Spectroscopy (EIS) the electrochemical behavior of the battery cell is modeled to get more in-depth knowledge of the electrochemical response of each component within the cell. By applying subsequently different voltages and thereby charge-states of the cathode a link to its capacity could be modeled. The Warburg-slope from the model was used to calculate the lithium diffusivity of the cathode thin film at different lithiation levels and compared to experimental results by Potentiostatic Intermittent Titration technique (PITT). Both values indicated lower values of the lithium diffusivity of the thin films as compared to previous studies in literature, indicating a strong interfacial contribution that cannot be neglected.

The observed capacity retention is compared to literature and found to be very high, outperforming polycrystalline thin films and being among the best performing particle cathodes.

As energy density is such an important feature in batteries, the electrochemical response of the additional discharge to $\text{Li}_2\text{Mn}_2\text{O}_4$, with a focus on structure stability and the proposed rapid capacity loss is elucidated. Overlithiating LiMn_2O_4 to obtain $\text{Li}_2\text{Mn}_2\text{O}_4$ gives a 3.8 V plateau which is hypothesized to be due to Li-Mn defect clusters. Cycling the 3 V plateau in the epitaxial thin films is shown to be stable with negligible capacity fade, indicating that the extra capacity at the 3 V plateau can be utilized effectively which allows doubling the capacity of $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode material.

Furthermore, cycling the 3 V plateau can rejuvenate any capacity loss occurring at the 4 V plateau. Allowing hardly any capacity fade over thousands of cycles possibly due to reverting back Li-Mn defect clusters. This allows this cathode material to be cycled deeper

Summary

for extensive lifetimes, allowing the use of the full 288 mAh/gram capacity by using both the 4 V and 3 V plateaus as opposed to only the 4 V plateaus with a capacity of 148 mAh/gram.

With the addition of a solid electrolyte a first step is taken to realize all-oxide full solid state batteries. $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ electrolyte thin films are synthesized, but exhibit TiOx impurities most likely due to lithium deficiencies. By combining the solid electrolyte with the LiMn_2O_4 cathode a nanocomposite can also be obtained. This nanocomposite suffers from the insulating electrolyte preventing connection of the cathode to the current collector, limiting charge-discharge behavior.

Finally, an all oxide full solid-state thin film battery was synthesized by combining the LiMn_2O_4 -cathode and $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -electrolyte with the anode $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Poor growth of the electrolyte combined with shorts between the anode and cathode prevented electrochemical performance. Further investigation and optimization on the growth of the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -electrolyte is required to enable a cyclable all oxide full solid-state battery.

This research demonstrates the scientific potential for epitaxial ceramic battery model systems, which new insights open up the possibility of using a wider potential range for $\text{Li}_x\text{Mn}_2\text{O}_4$ to increase the capacity almost twofold while achieving extensive lifetimes.

8 *Samenvatting*

Sinds hun introductie in 1990 zijn Lithium-ion batterijen dé bron van energie geworden voor vele mobiele en statische applicaties dankzij hun hoge energie en stroom dichtheid. Desondanks, gaat onderzoek hierop verder om deze eigenschappen van batterijen te verbeteren, alsmede ze veiliger en meer milieuvriendelijker te maken.

De drie meest gebruikte inschuif-kathode materialen zijn: olivijn LiFePO_4 , gelaagd LiCoO_2 en spinel LiMn_2O_4 . Hun verschillende lithium-diffusiewegen beïnvloeden de gebruiks- en levensduur van het gebruikte kathode materiaal. Verder bepaald dit de tussenlaag van de kathode met het elektrolyt en de stabiliteit daarvan, en daarmee, de veiligheid van de batterij. Het kathode materiaal LiMn_2O_4 staat bekend als een veelbelovend kathode materiaal door zijn 3D lithium-diffusiewegen en mogelijkheid tot het inschuiven van een 2^{e} lithium ion op 3 V. De literatuur laat daarentegen zien dat LiMn_2O_4 leidt aan het verliezen van capaciteit over het gebruik en slechte prestaties heeft tijdens laad-ontlaad cycli. Dit komt doordat Mn oplost en het materiaal een Jahn-Teller vervorming ondergaat. Er zijn verschillende strategieën gesuggereerd om dit tegen te gaan, maar een model systeem om de mechanismen te bestuderen ontbreekt.

Om een model systeem te creëren zijn zeer gecontroleerde dunne films gemaakt om een excellent model systeem te bieden om de mechanismen alsook limiterende factoren te bestuderen, inclusief de Li-ion diffusie, het Li-ion transport en het elektronisch transport. Gebruik makende van gecontroleerde kristalgroei-technieken zijn dunne kristallijne films aangebracht op substraten van Nb:SrTiO_3 met verschillende kristal oriëntaties waarmee de kristaloriëntatie van LiMn_2O_4 kan worden gecontroleerd. Dit staat toe om een unieke kijk te verkrijgen op de relatie tussen elektrochemie, contactoppervlakten en kristaloriëntatie,

welke niet te verkrijgen is in enkele kristallen noch polykristallijne deeltjes. Verder is dit tot nu toe slechts moeilijk te verkrijgen in gecontroleerde kristal-gegroeide films. Hoge ontladsnelheden met behoud van goede capaciteit en capaciteit over laad-ontlaad cycli zijn bereikt, wat laat zien dat het mogelijk is veel laad-ontlaad cycli door te maken zonder veel capaciteit verlies, in tegenstelling tot onderzoeken op polykristallijne deeltjes.

Door gebruik te maken van Elektrochemische Impedantie Spectroscopie (EIS) kan het elektrochemisch gedrag van de batterij-cel gemodelleerd worden om zo meer kennis te verschaffen over de elektrochemische processen van elk component binnen de cel. Wanneer de metingen verricht worden bij verschillende voltages, en daarmee de ontlad-stadia van de kathode, kan een link worden gelegd met zijn capaciteit. De helling van de Warburg-component in het model is gebruikt om de lithium diffusiteit van de kathode, bij verschillende lithium concentraties in de kathode, te berekenen en is vergeleken met experimentele resultaten van statisch Potentiaal tussentijdse Titratie Techniek (Potentiostatic Intermitted Titration Technique, PITT). Beide waarden voor lithium diffusiteit van de dunne films vallen lager uit dan voorgaande studies in de literatuur, wat een indicatie geeft dat een sterke contributie van het contactoppervlakte niet genegeerd kan worden.

Het behoud van capaciteit over cycli is vergeleken met literatuur waarden en laat erg hoge waarden zien. Het is beter dan die van polykristallijne dunne films en komt in de buurt van de beste kathodes bestaande uit stofdeeltjes.

Aangezien energiedichtheid zo'n belangrijke eigenschap van batterijen is, is het elektrochemisch gedrag bij het verder ontladen van LiMn_2O_4 naar $\text{Li}_2\text{Mn}_2\text{O}_4$ onderzocht. Hierbij is een focus gelegd op de stabiliteit van de structuur en de voorgestelde extreem snelle capaciteits-degradatie. Bij het cyclisch invoegen van een extra lithium-ion om van

LiMn_2O_4 naar $\text{Li}_2\text{Mn}_2\text{O}_4$ en weer terug te gaan wordt een extra voltage plateau bij 3.8 V geobserveerd. Deze wordt toegeschreven aan het ontstaan van clusters van Li-Mn defecten binnen de kathode. Laden en ontladen rondom het 3 V plateau laat stabiele capaciteit met verwaarloosbare capaciteitsverliezen zien van de dunne films met gecontroleerde kristalgroei. Dit geeft aan dat de extra capaciteit van het 3 V plateau straffeloos gebruikt kan worden waardoor effectief een verdubbeling van de capaciteit van het $\text{Li}_x\text{Mn}_2\text{O}_4$ kathode materiaal mogelijk is.

Verder leidt het laden en ontladen rondom het 3 V plateau tot het herstellen van enige capaciteitsverliezen bij het 4 V plateau. Hiermee is het mogelijk om zelfs na duizenden cycli verwaarloosbare verliezen te hebben in de capaciteit. Dit is waarschijnlijk mogelijk door het weer laten verdwijnen van de Li-Mn defecten in de kathode die in de loop van het gebruik ontstaan. Dit staat toe om dit kathode materiaal dieper te ontladen met langere levensduur waardoor de volle capaciteit van 288 mAh/gram van zowel het 4 V als het 3 V plateau gecombineerd gebruikt kan worden in tegenstelling tot de 148 mAh/gram van enkel het 4 V plateau.

Met het toevoegen van een vaste-stof elektrolyt is een eerste stap ondernomen tot het realiseren van volledig vaste-stof-batterijen bestaande uit oxidematerialen. Dunne films gemaakt uit het vaste-stof-elektrolyt $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ zijn gerealiseerd, maar bevatten TiO_x onzuiverheden, mogelijk door tekorten aan lithium. Door het vaste-stof-elektrolyt te combineren met de LiMn_2O_4 kathode kan een nanocomposiet worden verkregen. Deze composiet leidt alleen aan een isolerende laag elektrolyt richting de stroomcollector, waardoor laad-ontlaad gedrag wordt voorkomen.

Als laatste is een volledige vaste-stof-batterij van oxidische materialen gesynthetiseerd door de LiMn_2O_4 kathode te combineren met een $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ elektrolyt en een $\text{Li}_4\text{Ti}_5\text{O}_{12}$

anode. Door slechte kristalgroei van het elektrolyt gecombineerd met kortsluitingen tussen de anode en kathode kon elektrochemisch slechts zeer beperkt onderzocht worden. Verder onderzoek en geoptimaliseerde groei van het $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ -elektrolyt is nodig om volledig vaste-stof-batterijen bestaande uit oxidematerialen, elektrochemisch te onderzoeken.

Dit onderzoek laat het wetenschappelijk potentiaal van gecontroleerde kristalgroei van keramische materialen voor een batterij model systeem zien, wiens nieuwe inzichten leiden tot de mogelijkheid om een breder potentiaal gebied van de kathode $\text{Li}_x\text{Mn}_2\text{O}_4$ te gebruiken. Hierdoor kan de capaciteit van de batterij bijna verdubbeld worden terwijl ook nog een langere levensduur mogelijk is.

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Finally, a big thanks to my friends at Electric Superbike Twente, we have seen that motorcycles powered by batteries remain a challenge. May our friendship continue to electrify excellence and may you continue to win the MotoE.