

# Influence of experimental parameter on the Li-content of $\text{LiMn}_2\text{O}_4$ electrodes produced by pulsed laser deposition

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## Abstract

Thin film deposition by pulsed reactive crossed beam laser ablation has often advantages such as no need for annealing after deposition over conventional pulsed laser deposition. However, when depositing material from a target containing a low atomic mass component such as lithium, the resulting films are frequently sub-stoichiometric in the light elements. This is most probably due to scattering of the plasma plume in the crossed gas pulse, which creates a high local pressure. The light species are scattered more than the heavier elements, which leads to Li-deficiencies in the resulting film. Depositing lithium-spinels without the use of a crossed gas pulse is still strongly dependent on the applied background pressure. A background pressure below 10 Pa results also in lithium-deficient films. However, this is not due to scattering effects but very probably to the evaporation of lithium oxide from the growing film. These boundary conditions allow only a window of conditions for the growth of stoichiometric  $\text{LiMn}_2\text{O}_4$  films that is useful as test electrodes for Li-batteries research. A strong influence of the experimental parameters was observed. The films deposited at different background pressures and different substrate/target distances showed very different behaviors in the electrochemical measurements. Extraction and insertion of lithium was only detected for films deposited at a distance between 3 and 4 cm and at a background pressure of 20 Pa, whereas films deposited at other conditions did not show this electrochemical activity.

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## 1. Introduction

Pulsed laser deposition (PLD) is a promising technique to deposit thin films on various substrates, e.g., conducting or non-conducting, with very specific characteristics such as magnetic properties, electrochemical or catalytic activity. Highly sophisticated set-ups allow the fabrication of new materials that exhibit very specific properties in the area of chemistry and solid-state physics. In particular, PLD can be applied to synthesize well-defined thin electrodes. Electrodes used in research are mainly fabricated by electrochemical deposition processes, vapor deposition (without or with plasma assisting), thermal processes and microwave assisted processes [1]. The preparation of thin films by pulsed laser deposition may not be suitable on large industrial scales due to the high cost of the

laser and vacuum equipment. Nevertheless, PLD offers the high flexibility and precision needed for fundamental research and development of thin electrodes. It has long been shown that the growth of Li-spinels is possible by PLD on various substrates [2,3]. Careful adjustment of the experimental parameters allows to vary crystal properties such as preferred orientation, film thickness, stoichiometry, formation of multilayers and content of metals such as aluminum and cobalt stabilizing the lattice. The deposition of electrochemically active  $\text{LiMn}_2\text{O}_4$  thin films by PLD on stainless steel has already been reported [2,3], and a strong influence of the deposition conditions on the lithium stoichiometry was shown.

Li-batteries have found a very broad and promising application in modern technology [4,5]. They are used due to their high energy density as rechargeable power source in mobile phones, portable computers, digital cameras and other small electronic devices, which require the usage of small batteries. The technical requirements for Li-batteries, such as fast charge and discharge, long cycle time and chemical

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stability require a good understanding of the kinetics of the Li-transfer in the system such as the diffusion and migration of the Li-ion through active materials and the electrolyte, the insertion and de-insertion of the ion, and the influence of lattice defects on the charge/discharge behavior in order to facilitate the optimization of the batteries to enhance the performance. So far, the migration and diffusion of lithium ions is well described. The process is relatively slow and can be fastened by usage of small particle size active materials, and the utilization of thinner layers to lower the resistance of the electrolyte. To minimize the reactions with the electrolyte, the effective surface area of the electrodes is normally reduced. Thus, the interfacial reaction could therefore become the rate-controlling step for the entire electrochemical process, which is directly related to the performance of the battery. For a better understanding of interface processes, well-defined crystalline model systems are advantageous. The use of  $\text{LiMn}_2\text{O}_4$  films in pure form or doped with metals to form quaternary spinel phases, for example:  $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$ ,  $M = \text{Co}, \text{Cr}, \text{Ni}$  [6] is one possible direction for the investigation. Materials such as  $\text{LiMn}_2\text{O}_4$  form a spinel structure, whose reaction sites are very well defined [7]. Spinel structures such as  $\text{LiMn}_2\text{O}_4$  are therefore very suitable as electrode material for the investigation of the electrochemical processes involved in Li-batteries.

## 2. Experimental

### 2.1. Pulsed laser deposition

The deposition experiments were carried out in a standard vacuum chamber, which allows background pressures of  $\text{O}_2$  between 10 and 30 Pa. The distance between the substrate and the target was varied between 3 and 7 cm in steps of 1 cm. All deposition experiments were performed with a KrF excimer laser (Lambda Physik LPX 100), with a pulse width of 20 ns and a repetition rate of 10 Hz. The fluence of the laser beam was kept constant between 4.2 and 4.6  $\text{J}/\text{cm}^2$  for all experiments. The target material was fabricated by sintering a stoichiometric oxide of  $\text{LiMn}_2\text{O}_4$  at 1023 K for 30 min. The composition of the films was analyzed by Rutherford backscattering spectrometry (RBS), for the detection of manganese and oxygen) and elastic recoil detection analysis (ERDA), for the determination of the Li/Mn ratio, while the crystallinity was analyzed by X-ray diffractometry on a Siemens D-500 X-ray diffractometer. The films on polished titanium foil (Goodfellow, average roughness 25 nm) were also characterized by cyclic voltammetry after determining the crystallinity with XRD. The films used for RBS/ERDA were deposited on Si(1 0 0) under the same experimental conditions.

### 2.2. Cyclic voltammetry

Lithium foil (Aldrich), ethylene carbonate (EC; Merck), propylene carbonate (PC; Fluka) and  $\text{LiPF}_6$  (Aldrich) of highest available quality were used as received. The preparation of the electrolyte solutions and the assembly of the cells were performed in an argon-filled glove box with water and oxygen

contents of less than 5 ppm. The thin oxide films on the titanium samples substrate were vacuum-dried at 393 K overnight before electrochemical characterization.

Cyclic voltammetry (CV) experiments were performed in a two-electrode arrangement as described in detail elsewhere [8]. A Li-foil served as counter and reference electrode. Therefore, all potentials will be referred to metallic lithium as reference ( $\text{Li}/\text{Li}^+$ ). The CV measurement was started at an open circuit potential (OCP; normally between 2.9 and 3.1 V) and continued between 3.5 and 4.3 V versus  $\text{Li}/\text{Li}^+$ . All measurements were carried out at 298 ( $\pm 0.1$ ) K with a scan rate of 0.1 mV/s.

## 3. Results and discussion

### 3.1. Rutherford backscattering spectrometry and X-ray diffraction

$\text{LiMn}_2\text{O}_4$  forms a spinel structure with a  $Fd\bar{3}m$  space group and lattice parameter  $a = 8.239 \text{ \AA}$ . Fig. 1 shows the X-ray diffraction spectrum of the  $\text{LiMn}_2\text{O}_4$  film (nominal composition) deposited on a titanium substrate. The peaks attributed to the spinel structure are clearly visible [9–12]:  $18.4^\circ$  for (1 1 1),  $35.6^\circ$  for (3 1 1) and  $43.6^\circ$  for (0 0 4). The peak at  $37.78^\circ$  for (2 2 2) is visible only as shoulder of the strong peak at  $38.4^\circ$ . The peaks marked with an asterisk in Fig. 1 can be attributed to the substrate and titanium. These peaks are detected for all films deposited at all distances and pressures. Ti is polycrystalline with (1 0 0) preferentially parallel to the surface of the substrate.

In Fig. 2, the spectrum and the analysis of the RBS measurements of a film deposited on a silicon(1 0 0) substrate is shown. The films were deposited at a laser fluence between of 4.3  $\text{J}/\text{cm}^2$ , a substrate temperature of  $\approx 773 \text{ K}$  and an oxygen background pressure of 20 Pa. The number of pulses is 18,000. The films reveal a sub-stoichiometric content of oxygen and a slight deficiency of lithium. The calculated composition of the film corresponds to  $\text{Li}_{0.96}\text{Mn}_2\text{O}_{3.74}$ . However, it should be possible to increase the oxygen content in the film by post-deposition annealing in an oxygen atmosphere. Since lithium is much lighter than manganese or oxygen it can be more easily

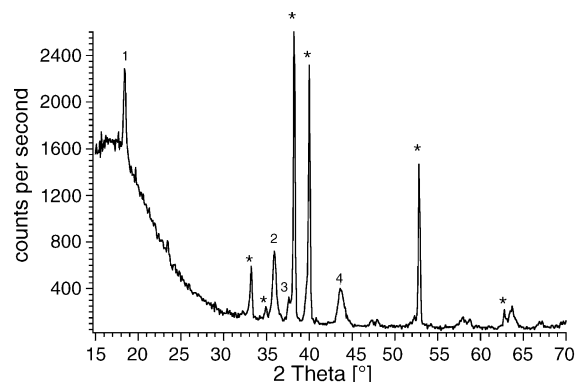


Fig. 1. XRD spectrum of a  $\text{LiMn}_2\text{O}_4$  (nominal composition) film deposited on a titanium substrate. The signals that can be attributed to a spinel structure are:  $18.4^\circ$  for (1 1 1) (1),  $35.6^\circ$  for (3 1 1) (2),  $37.78^\circ$  for (2 2 2) (3) and  $43.6^\circ$  for (0 0 4) (4) orientation. The peaks marked with an asterisk can be assigned to the titanium substrate.

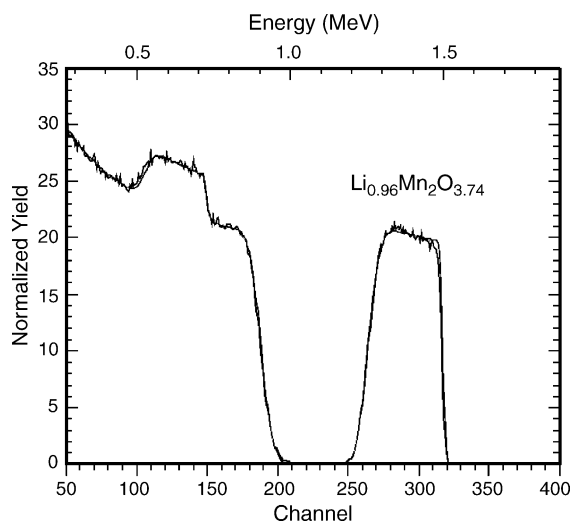


Fig. 2. RBS measurements of  $\text{LiMn}_2\text{O}_4$  thin films deposited on  $\text{Si}(1\ 0\ 0)$  with laser fluences of 4.3 and 4.5  $\text{J}/\text{cm}^2$ , a substrate temperature of  $\approx 773\ \text{K}$ , and an oxygen background pressure of 20 Pa; 18,000 pulses were applied.

scattered. Therefore, it is likely that less Li compared to heavier atoms reach the substrate surface, which yields films with lower Li-content. Rougier et al. [2,10] examined the Li-content of films grown by pulsed laser deposition using stoichiometric targets and targets with an excess of lithium. In their work, it was demonstrated that a stoichiometric target and a larger substrate/target distance results in lithium-deficient films, while a target with excess of Li and a short substrate/target distance yields films with lithium excess. The substrate used in their studies was stainless steel, which was heated to 873 K in an oxygen atmosphere between 4 and 10 Pa. They also demonstrated the presence of a  $\text{Mn}_2\text{O}_3$  impurity phase for the lithium-deficient films. This impurity could not be detected in our experiments since the expected corresponding peaks in the XRD spectrum of  $\text{Mn}_2\text{O}_3$  are probably overlapped by the peaks attributed to titanium and titanium oxide. The authors concluded that the content of lithium in the film drops with increasing substrate/target distance. The influence of different excess ratio (between 5 and 15%) of lithium in the target on the Li/Mn ratio in the resulting film was also studied [13]. The optimum content of lithium in the target was found to be 15%. These results suggest that it is advantageous to apply a target with an excess (up to 15%) of lithium rather than a stoichiometric one.

The influence of the substrate temperature and the background pressure on the stoichiometry of the film was studied in detail by Morcrette et al. [14,15]. In this study,  $\text{LiMn}_2\text{O}_4$  was deposited from stoichiometric targets onto Pt, Si and  $\text{MgO}$  substrates. The laser power of a quadrupled Nd:YAG laser with a pulse width of 7 ns was varied between 50 and 200  $\text{MW}/\text{cm}^2$ . A large loss of lithium was detected when heating the substrate above 773 K in an oxygen atmosphere of 10 Pa. For a substrate temperature of 773 K, an excess of lithium was found for films deposited at pressures above 20 Pa, whereas pressures below 20 Pa led to lithium-deficient films. The group suggested the optimum conditions to be a background pressure of 20 Pa, a

substrate temperature of 773 K, and a substrate/target distance of 4 cm.

These experimental conditions are very close to those applied in our experiments, except for the different laser source (a KrF excimer laser with a pulse length of 20 ns and an emission wavelength of 248 nm compared to a Nd:YAG laser with a pulse length of 7 ns and an emission wavelength of 266 nm in the study mentioned above). Nevertheless, we were unable to produce stoichiometric spinel films until now. The Li/Mn ratio in our films is still slightly lower than the value reported by Morcrette et al. [14,15]. The only other difference is the substrate material, i.e., we apply Ti while materials like stainless steel and platinum were chosen in [10,11,14–18].

Fig. 3 shows the Li/Mn ratio in the film calculated from the RBS/ERDA measurements as a function of the substrate temperature for samples deposited at a background pressure between 10 and 30 and 0.1 Pa on different substrates.

The data suggest a weak influence of the substrate temperature on the Li/Mn ratio. However, this is in contradiction with the general concept of lithium-loss with increasing temperatures. Considering the XRD patterns of the films, one can conclude that the films grown at lower background pressures (open and full circles in Fig. 3) and high substrate temperature do not have a spinel structure, while the films deposited under higher pressure (rhombus in Fig. 3) and lower temperature exhibit peaks that can be assigned to a Li-spinel structure.

The films deposited at higher temperatures and lower pressures revealed a chemical composition that is close to the nominal composition Li:Mn:O 1:2:4 of  $\text{LiMn}_2\text{O}_4$  but did not show an electrochemical activity in the CV measurements. This is most probably related to the absence of spinel phase. The XRD data revealed no reflexes that could be assigned to the spinel structure, but it was also not possible to assign the detected reflexes to other phases, e.g., Mn or Li oxides, because for all possible candidates a pronounced overlap with the substrate peaks is present.

We therefore can conclude that films deposited under high pressure and relatively low substrate temperatures would be more active for Li extraction. The CVs performed at samples prepared at very low pressure confirm this assumption since almost no extraction of lithium was detected. In which form lithium is bound in these films is not yet clear.

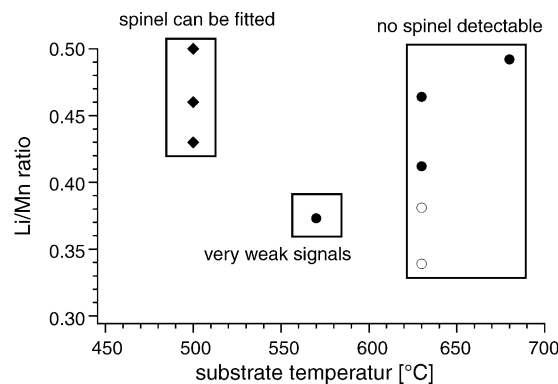


Fig. 3. Overview of Li/Mn ratio calculated from the RBS and ERDA data (◆) high pressure: 10–30 Pa and (● and ○) low pressure: 0.1 Pa).

### 3.2. Cyclic voltammetry

Cyclic voltammetry was applied to investigate the influence of the PLD parameters on both the reversibility and the kinetics of the  $\text{LiMn}_2\text{O}_4$  electrode. The CV experiments were performed in EC/PC 1:1 (volume ratio) with 1 M  $\text{LiPF}_6$  as electrolyte solution. Fig. 4 shows the first 19 cycles of a  $\text{LiMn}_2\text{O}_4$  film deposited with a target–substrate distance of 3 cm and a background pressure of 20 Pa. The thickness of the film is approximately 700 nm. In the first cycle, the oxidative peak starts around 3.6 V – indicating extraction of lithium ions and an expected solid electrolyte interphase (SEI) formation – obviously under formation of a variety of reduction products and, possibly, structural transformation. This would explain the evident difference of the first cycle with respect to the following cycles. The oxidative and reductive peaks – even in the following cycles – due to the lithium extraction and insertion showed one broad peak, which indicates that the spinel is non-stoichiometric.

Fig. 5 shows the CV of a film deposited at a substrate/target distance of 4 cm at the same background pressure, laser fluence, and number of pulses. The thickness of the film is approximately 300 nm. With a thinner layer two significant changes in the CVs are visible. Two oxidative current peaks arise with maxima at 4.05 and 4.2 V, respectively, and the reductive peaks are at 3.6 and 3.9 V, respectively. One can attribute these peaks to the different stages of lithium ion insertion and extraction from/into the  $\text{LiMn}_2\text{O}_4$  (nominal composition) layer. This significant difference to the thicker films indicates that the thinner layer is closer to the nominal composition of the spinel,  $\text{LiMn}_2\text{O}_4$ . It has been reported previously [2,19–21] that a variation in the Li-spinel composition has a pronounced influence on the electrochemical behavior in lithium batteries. However, with increasing cycle number the current slightly decreases, which suggests that

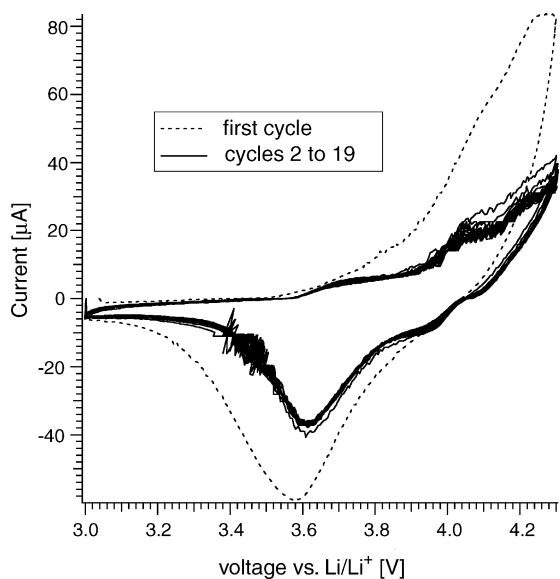


Fig. 4. Cyclic voltammogram of a  $\text{LiMn}_2\text{O}_4$  (nominal composition) film deposited on titanium substrate at a distance of 3 cm from the target.

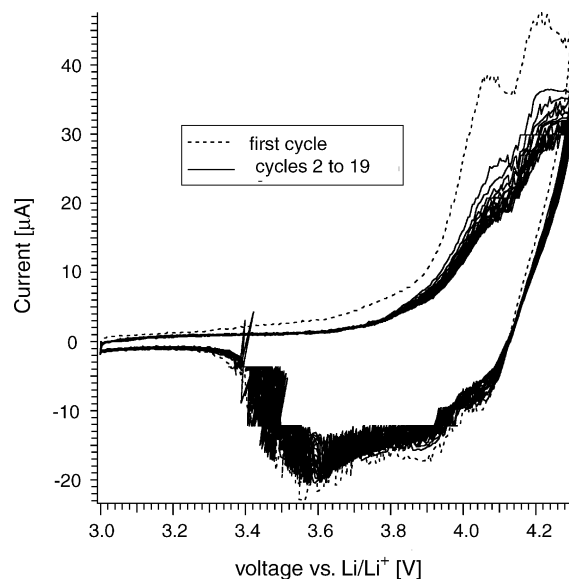


Fig. 5. Cyclic voltammogram of a  $\text{LiMn}_2\text{O}_4$  (nominal composition) film deposited on titanium substrate at a distance of 4 cm from the target.

either the formed SEI film prevents a fast lithium extraction/insertion and/or the structure of the material changes continuously.

Cyclic voltammetric measurements performed on films grown at longer distances and at a background pressure of 10 and 30 Pa, respectively, did not show this behavior. Electrochemical activity could be shown but peaks did not appear in the expected potential range. In fact, CVs performed on an uncoated titanium substrate showed a high electrochemical activity of the titanium (or titanium oxide surface), which seems to overlap with the peaks generated by the  $\text{Li}_x\text{Mn}_2\text{O}_4$ . A slight lithium deficiency and a strong sub-stoichiometry of oxygen resulting in another crystal structure could be the reason for this. The low signal to noise ratio in Fig. 3 and especially in Fig. 4 are currents from the electrochemical reactions of the electrolyte in solution in contact with the non-coated surface of the titanium substrate.

### 4. Conclusions

$\text{LiMn}_2\text{O}_4$  films were deposited on titanium and silicon substrates to investigate the influence of experimental parameters, such as background pressure and substrate/target distance, on the stoichiometry of the film and electrochemical activity of the films. The films deposited with a very low background pressure exhibit a Li/Mn ratio of almost 0.5, whereas the films grown under experimental conditions as suggested in the literature were slightly lithium-deficient (Li/Mn between 0.43 and 0.5) but strongly oxygen-deficient. However, very low pressures and high substrate temperatures do not lead to the formation of a spinel phase that can be detected by X-ray diffraction and show only very poor (de)-insertion properties for lithium. Films deposited at higher pressures and lower substrate temperatures, which were also suggested in the literature, exhibit the presence of a Li-spinel phase, which is electrochemically active but which is lithium

and oxygen-deficient. We can conclude from these results that the stoichiometry of lithium and oxygen in  $\text{LiMn}_2\text{O}_4$  thin films deposited by PLD is highly sensitive to the experimental parameters applied and that these parameters may not be transferable from one set-up to another.

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