



Experimental and *ab initio* investigations on textured Li–Mn–O spinel thin film cathodes



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ABSTRACT

This paper describes the tailored preparation of nearly identical lithium–manganese–oxide thin film cathodes with different global grain orientations. The thin films were synthesized by rf magnetron sputtering from a LiMn_2O_4 -target in a pure argon plasma. Under appropriate processing conditions, thin films with a cubic spinel structure and a nearly similar density and surface topography but different grain orientation, i.e. (111)- and (440)-textured films, were achieved. The chemical composition was determined by inductively coupled plasma optical emission spectroscopy and carrier gas hot extraction. The constitution- and microstructure were evaluated by X-ray diffraction and Raman spectroscopy. The surface morphology and roughness were investigated by scanning electron and atomic force microscopy. The differently textured films represent an ideal model system for studying potential effects of grain orientation on the lithium ion diffusion and electrochemical behavior in LiMn_2O_4 -based thin films. They are nearly identical in their chemical composition, atomic bonding behavior, surface-roughness, morphology and thickness. Our initial *ab initio* molecular dynamics data indicate that Li ion transport is faster in (111)-textured structure than in (440)-textured one.

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1. Introduction

In the last years there has been an increasing interest in electrical energy storage. The commercial requirements are clear and unambiguous: the storage solutions should be powerful, compact and safe. Not only in the case of consumer electronics like cellular phones or tablet PCs but also in the field of self-sustaining microsystems or sensors it is important to search more intensively for smaller electrochemical storage devices. Thin film technology is an outstanding method to combine fundamental research on the one hand with device development on the other hand. Today the most commercially available lithium ion batteries are still based on LiCoO_2 as standard cathode material [1,2]. It has a layered structure (space group: $R\bar{3}m$, structure type: $\alpha\text{-NaFeO}_2$) and exhibits practical reversible capacities of approximately 140–160 mAh/g [3]. However industry is searching for other, more suitable cathode materials, because LiCoO_2 is toxic and expensive [4] and shows problems with its stability during overcharge, which is adverse for safety reasons [5]. Other cathode materials, that could be promising candidates to avoid these disadvantages, are lithium manganese oxide based cathodes. A well-known representative of the Li–Mn–O compounds is the cubic- LiMn_2O_4 spinel (space group: $Fd\bar{3}m$, structure

type: $c\text{-MgAl}_2\text{O}_4$) (Fig. 1). This structure has a face-centered cubic oxygen sub lattice, in which the oxygen ions occupy the 32e Wyckoff positions. The Mn ions occupy 50% of the octahedral 16d vacancies and the lithium ions fill 25% of the tetrahedral 8a sites. Through this special cation-arrangement LiMn_2O_4 is known to be a more stable structure in comparison to the layered structures [3]. During the charge and discharge process the Mn-ions change their oxidation state between Mn^{3+} and Mn^{4+} and vice versa. The average manganese oxidation state of the stoichiometric compound is $\text{Mn}^{+3.5}$. In this kind of materials it is possible to have Mn^{3+} -ions in an octahedral oxygen arrangement, which can cause problems with the Jahn-Teller distortion [6]. During discharge, especially below the 3 V regions, this induces an irreversible phase transformation from the cubic spinel to a tetragonal- $\text{Li}_2\text{Mn}_2\text{O}_4$ phase, which causes significant capacity reduction during cycling [7]. With an adequate choice of the voltage window this problem can be minimized [8]. In the past there was a lot of work carried out on cubic- LiMn_2O_4 spinel thin films synthesized by magnetron sputtering [9–13], laser deposition [14–20] or electron beam deposition [21]. All of these articles deal with LiMn_2O_4 -based thin film cathodes, but there is no report about the independent structure and surface topography texture variations. Therefore in this work, a model system of two nearly identical cubic spinel thin films, with respect to their thin film phase, elemental composition, chemical bonding behavior, surface morphology and mass density but with different average grain orientations were

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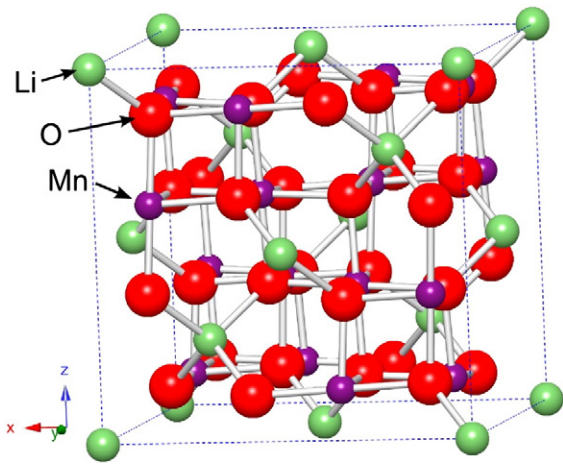


Fig. 1. (color online) Lattice structure of *c*-LiMn₂O₄. Oxygen ions are arranged in a ccp sub lattice on the 32e positions. Manganese and lithium ions occupy 50% of all octahedral (16d) and 25% of all tetrahedral (8a) sites, respectively.

developed, allowing the investigation of the texture–electrochemistry relationships.

2. Experimental methods

To produce a uniform surface, circular stainless steel substrates with a diameter of 12 mm and a thickness of 0.5 mm were first grinded with different abrasive papers (companies: Hermes Schleifmittel GmbH and ATM GmbH) with a stepwise decreasing grain size (P800, P1000, P1200, P2400 and SiC-P4000). Then three wet polishing processes by a diamond suspension with an overall grain size of 3 and 1 μm as well as 60 nm (ATM GmbH) were employed to finish the procedure. Each grinding and wet polishing step was carried out for 2 min each under a load pressure of 200 kPa on a Rubin 520 polishing device (ATM GmbH). This produced a polished surface on the stainless steel discs. After polishing, all samples were cleaned at room temperature for 7 min in an ultrasonic bath consisting of high purity acetone. To remove remaining molecular adsorbates like hydrocarbons or moisture, the surface of all substrates was additionally ion-etched in a pure argon plasma at 500 W rf power before each deposition process. The whole

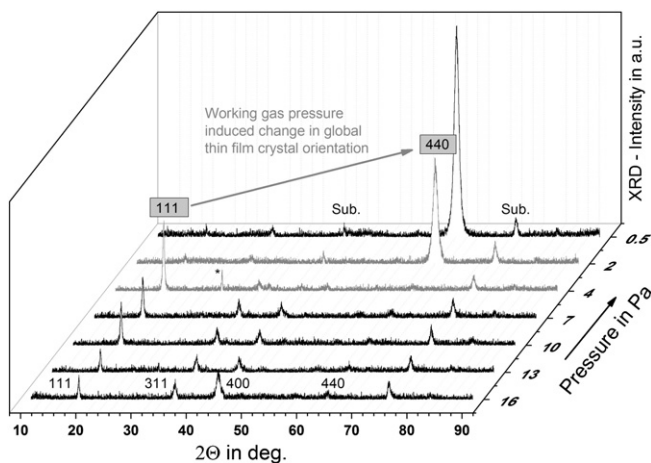


Fig. 2. XRD-patterns of the synthesized thin film cathodes after the stepwise thermal annealing to 600 °C. All thin films, which were sputtered between 16.0 and 4.0 Pa argon working gas pressure show a (111)-reflection, whereas all thin films, which were sputtered between 2.0 and 0.5 Pa mainly crystallize with a (440)-orientation. With decreasing working gas pressure, the intensities of both reflexes increase.

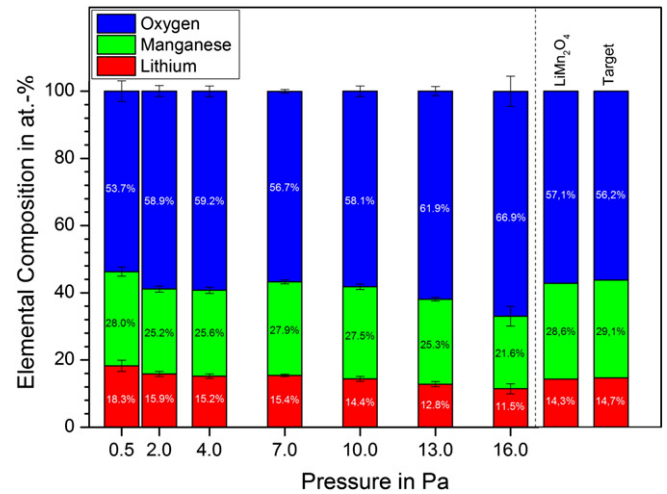


Fig. 3. (color online) Elemental composition in atomic percent of the as deposited films, which were synthesized at argon working gas pressures between 0.5 and 16.0 Pa. The stoichiometry of the 2.0 and 4.0 Pa films is nearly identical. The composition of the target is best reproduced between 7.0 and 10.0 Pa. In addition the composition of the stoichiometric LiMn₂O₄-phase is given on the right side. With increasing working gas pressure a slow decrease in lithium content is observed.

plasma-etching was carried out for 10 min and removed approximately 15 nm of the substrate surface. Li–Mn–O thin film deposition was carried out by rf magnetron sputtering under pure argon atmosphere in a Leybold Heraeus Z550 physical vapor deposition facility. A LiMn₂O₄-target with a diameter of 7.6 cm and a thickness of 6.3 mm was used (purity: 99.9%, company: MaTeck GmbH Germany). A piece at the edge of the target gave a chemical composition of (Li:Mn:O = 14.7 at.-%:29.1 at.-%:56.2 at.-%) close to the expected stoichiometric composition (1:2:4 = 14.3 at.-%:28.6 at.-%:57.1 at.-%). The Li/Mn ratio of the deposited films was determined on Si substrates by inductively coupled plasma optical emission spectroscopy (ICP-OES; OPTIMA 4300 DV Perkin-Elmer) and the oxygen content was achieved by carrier gas hot extraction (CGHE; TC 600 Leco). During the deposition process the target power was adjusted to 100 W (~2.2 W cm⁻²) and a systematic parameter study between 0.5 and 16.0 Pa working gas pressure was carried out. The base chamber pressure before deposition was approximately 7×10^{-5} Pa. Film thickness was determined with a surface profilometer Tencor P-10.

To improve the crystallinity of the films, a post deposition annealing process was carried out in a box-type furnace under air atmosphere (~100 kPa). Four temperatures (300 °C, 400 °C, 500 °C and 600 °C) were investigated by a step by step annealing. After each temperature step, with an annealing time of 30 min, the samples were removed from the furnace and rapidly cooled down in stagnant air to room temperature within approximately 7 min to prevent internal film cracking or delamination at longer annealing times.

X-ray diffraction (XRD) was carried out at room temperature between $2\theta = 10^\circ$ and 90° using a Seifert PAD II in Bragg-Brentano geometry with Cu-K_{α1} radiation at $\lambda_{\text{XRD}} = 0.154$ nm (40 kV at 30 mA). Raman spectra were recorded with a micro-Raman spectroscopy Renishaw 1000 system. As exciting light source a Soliton Ar-ion laser (wavelength: $\lambda_{\text{Laser}} = 514.5$ nm, maximum output power: 23 mW) was used. To minimize the risk of possible phase transformations during the measurements by laser annealing, induced by the exciting laser light [22], the laser power was reduced by 10% with an additional transmission filter. Surface morphology and roughness measurements were carried out with an atomic force microscope (AFM; NanoScope) in tapping mode over an area of $10 \times 10 \mu\text{m}$ at three different sample positions, and a scanning electron microscope (SEM; Philips Typ XL 30S) with an acceleration voltage of 15 kV. X-ray reflectivity measurements (XRR)

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