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Influence of the substrate material on the properties of pulsed laser deposited thin $Li_{1+x}Mn_2O_{4-\delta}$ films

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ABSTRACT

Thin $\text{Li}_{1+x}\text{Mn}_2\text{O}_{4-\delta}$ films were deposited on several substrate materials (stainless steel, p-doped silicon and glassy carbon) by pulsed laser deposition. To obtain the correct thin film stoichiometries, targets with a different amount of excess lithium were required (Li_{1.03}Mn₂O₄ + xLi₂O; x = 2.5 and 7.5 mol%). The resulting polycrystalline thin films were characterized with respect to their morphology and electrochemical activity. It was found that only thin Li_{1+x}Mn₂O_{4-δ} films deposited on stainless steel and glassy carbon showed the typical insertion and deinsertion peaks of Li⁺ during cycling.

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1. Introduction

The LiMn₂O₄ spinel is a promising cathode material for rechargeable lithium-ion batteries and considered as an alternative to the nowadays used LiCoO₂. The Li–Mn–O spinel is also cheaper and non-toxic compared to the LiCoO₂. The commonly used electrodes, which are composite materials, are consisting of binder compounds and additives such as carbon. A fundamental study of the detailed reaction mechanisms at these composite electrodes during charging and discharging is difficult because the influence of the other (inactive) materials may affect the results of the electrochemical characterization. Therefore it is advantageous to have model electrodes free of conductive carbon and binder materials. To prepare such model electrodes we used pulsed laser deposition (PLD) to deposit the Li-spinel for electrochemical characterization on several conductive substrates.

In our study the $Li_{1+x}Mn_2O_{4-\delta}$ spinels were deposited on three different substrates (stainless steel, glassy carbon, and p-doped silicon) by pulsed laser deposition. The substrate materials for our study were selected with respect to (a) good conductivity, (b) chemical and electrochemical stability (inertness in the desired potential range), and (c) high surface quality, to obtain films with

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high surface quality. To obtain for all films on the different substrates the same nominal Li_{1+x}Mn₂O_{4- δ} composition, targets with different amounts of added Li₂O (Li_{1.03}Mn₂O₄ + xLi₂O (*x* = 2.5 and 7.5 mol%, respectively)) were used. The literature reports Li_{1+x}Mn₂O_{4- δ} deposited on, e.g., silicon [1-4], indium tin oxide (ITO) [5], titanium foil [1], Pt [6], and stainless steel (SS) [3,7–9]. A disadvantage of an uncoated titanium foil as a substrate material was the high electrochemical activity of the foil itself [1]. Until now, pulsed laser deposition of the Li_{1+x}Mn₂O_{4- δ} spinel on glassy carbon was not reported.

2. Experimental

2.1. Film preparation and structural characterization

The Li_{1+x}Mn₂O_{4- δ} films were prepared by pulsed laser deposition (KrF, λ = 248 nm, 10 Hz, 4.0–4.3 J cm⁻²) in 20 Pa oxygen background pressure with an average film thickness of 300 nm. The fixed substrate-target distance was 4 cm, and the deposition temperature was kept for all experiments at 500 °C. After the deposition, the films were cooled in 20 Pa oxygen within 30 min to room temperature.

Three different substrates were used: stainless steel (SS, Austenitic, Typ304, Tokyo Stainless Kennma Co.), glassy carbon (GC, SIGRADUR G, HTW, Thierhaupten, Germany), und p-doped silicon (p-Si; (100) oriented; boron doped, $\sigma < 0.01 \Omega$ cm,



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CrysTec, Berlin). Depending on the substrate material different target compositions were used to obtain the same nominal film stoichiometry of $\text{Li}_{1+x}\text{Mn}_2\text{O}_{4-\delta}$ (x = 0.04 - 0.06, $\delta = 0.05 - 0.59$). The targets were prepared by mixing $\text{Li}_{1.03}\text{Mn}_2\text{O}_4$ (99.7% purity, Honeywell, Li/Mn = 0.515) with different amounts of Li₂O (2.5 and 7.5 mol% Li₂O, respectively). Afterwards the mixed powders were pressed in rods with 400 MPa and subsequently sintered at 750 °C in oxygen for 10 h.

By using various methods the thin films were characterized with respect to: (a) stoichiometry combining Rutherford backscattering spectrometry (RBS) with elastic recoil detection analysis (ERDA, LiNbO₃ standard), (b) crystallinity (X-ray diffraction with Siemens D-500 X-ray diffractometer, Cu K α), and (c) surface morphology (scanning electron microscopy (SupraZeiss VP55, SEM, SE2 detector, 3 kV)).

2.2. Electrochemical characterization

The electrochemical cells consisted of Li_{1+x}Mn₂O_{4- δ} films as cathode materials and a lithium metal foil (Aldrich) as anode material separated by a glass fiber separator. The films were cycled in the potential range from 3.5 to 4.4 V (vs. Li/Li⁺). A LiClO₄ in propylene carbonate solution (1 M, ca. 600 ppm H₂O) was used as the electrolyte. The cells were assembled in a glovebox (content of H₂O of <0.1 ppm, O₂ of ~0.6 ppm). By using cyclic voltammetry the thin films were analyzed with respect to their charge/discharge behaviour. After cycling the thin films were again characterized with respect to the surface morphology.

3. Results and discussion

3.1. Film characterization: composition, crystallinity and surface morphology

For the deposition of LiMn₂O₄ films on different substrates, targets with an excess of Li to the nominal composition of Li₁₀₃Mn₂O₄ prepared by adding Li₂O were used: 2.5 mol% Li₂O for glassy carbon and p-doped silicon, and 7.5 mol% Li₂O for stainless steel. The resulting film stoichiometries (on stainless steel: Li_{1.04}Mn₂O_{3.41}; on p-doped silicon: Li_{1.06}Mn₂O_{3.95}; on glassy carbon: Li_{1.06}Mn₂O_{3.8}) show in general oxygen and lithium deficiencies, which result from a noncongruent deposition of $Li_{1+x}Mn_2O_{4-\delta}$ [1,10]. A possible reason for the measured lithium deficiency could originate from scattering of lithium by heavier ions or oxygen molecules during ablation and/or backscattering or sputtering of the lithium ions from the substrate/film surface [1]. The highest oxygen and lithium deficiency compared to the starting target composition is observed for films on stainless steel. Films on p-doped silicon and glassy carbon show a lithium deficiency of 1.9% as compared to films on stainless steel (11.7%). All substrates will have oxygen containing groups at the surface. But we do not believe that the difference is due to a reaction between substrate and oxygen, but due to different adhesion coefficients.

The X-ray pattern of the approximately 300 nm thick $Li_{1+x}Mn_2O_{4-\delta}$ films are shown in Fig. 1a. The measured reflexes correspond to crystalline $Li_{1+x}Mn_2O_{4-\delta}$. The highest crystallinity is obtained for films on p-doped silicon, while the lowest crystallinity was detected for films on glassy carbon, which itself has a short range order. Films on (1 0 0) p-doped silicon grow with a preferred (1 1 1)-orientation [6], whereas $Li_{1+x}Mn_2O_{4-\delta}$ films on glassy carbon and stainless steel have less (1 1 1) orientation than the films on p-Si. These films are more polycrystalline. In Fig. 1b the (1 1 1) reflex of $LiMn_2O_4$ for different substrate materials is shown. The observed shift in the corresponding lattice constant compared



Fig. 1. X-ray pattern of thin Li_{1+x}Mn₂O_{4- δ} films (a) on stainless steel (SS, top), on glassy carbon (GC, middle), and on p-doped silicon (p-Si, bottom) substrates. The pattern of the substrate materials are marked with open symbols. The dependence of the shift of the (1 1 1) reflex of Li_{1+x}Mn₂O_{4- δ} on the substrate material is shown in the enlargement (b).

to the expected literature value of 8.248 Å [11] suggests tensile (p-Si, 8.235 Å) and correspondingly compressive stress (GC, 8.267 Å; SS, 8.292 Å) in the deposited films. The best lattice match is obtained for films on p-Si. In the case of the (1 0 0) unit cell of p-Si the (1 1 1) growth orientation of the film is preferred. The calculated lattice mismatch is 7.2%, which could explain the tensile stress in the spinel.

The Li_{1+x}Mn₂O_{4- δ} films show a dependence of the surface morphology on the used substrate material (see Fig. 2a–c). Films on polycrystalline stainless steel substrate reveal an irregular surface morphology with rod and flake like shaped particles. Dependent on the shape of the formed grain boundaries during heating in 0.2 mbar, the thin films on stainless steel pieces have partially obtained different growth orientation of the formed particles. A more homogenous surface morphology with rod like particles is observed for films on glassy carbon (with several bigger particles)



Fig. 2. SEM pictures of the surface morphology of $Li_{1+x}Mn_2O_{4-\delta}$ thin films on (a) stainless steel, (b) glassy carbon, and (c) p-doped silicon before cycling.

and for films on p-doped silicon. However, the lowest adhesion to the substrate is observed for thin films on glassy carbon. Occasionally, after the deposition the films peeled off the substrate easily.

3.2. Electrochemical characterization of the thin films

The thin Li_{1+x}Mn₂O_{4- δ} films on the different substrates were tested as cathode materials and charged and discharged between 3.5 and 4.4 V versus metallic lithium in the LiClO₄/PC electrolyte. During the charging (oxidation process) the lithium ions are extracted in two reversible steps from the spinel and λ -MnO₂ is formed [5,12] (see following equations):

 $LiMn_2O_4 \rightleftharpoons \frac{1}{2}Li^+ + \frac{1}{2}e^- + Li_{0.5}Mn_2O_4$

 $Li_{0.5}Mn_2O_4 \rightleftharpoons \frac{1}{2}Li^+ + \frac{1}{2}e^- + 2\lambda$ -MnO₂

During the discharging (reduction) process lithium ions are reinserted. The cyclic voltammograms of the films on stainless steel and glassy carbon substrates are shown in Fig. 3a and b. Films on pdoped silicon reveal no electrochemical activity. That could be due to a poor electrical contact between the film and the substrate, because in experiments with an additional conductive metallic layer between the film and the substrate (Pt and Au, respectively), the typical charge and discharge behaviour of LiMn₂O₄ was observed. For Li_{1+x}Mn₂O_{4- δ} films on stainless steel and glassy carbon the typical oxidation and reduction peak pairs corresponding to the two lithium deinsertion and insertion steps are observed in contrast to films deposited on p-doped silicon. The position of the peak maxima match well with the literature data [13]. The obtained maxima of the normalized current density (with respect to the film thickness) for films on stainless steel and glassy carbon are in the range of 70–80 μ A cm⁻² μ m⁻¹ for the first cycles. Dependent on the variation of the surface morphology for films on stainless steel, a larger variation of the peak current density is detected. This could be due to variations of active surface area (surface wetted with the electrolyte), which is expected to influence the insertion and deinsertion of the lithium ions [14]. It is noted that in our study the current density is given with respect to the geometrical surface area and the thickness of the film.

The observed moderate decrease in the charge capacity of the spinel layers on stainless steel and glassy carbon during cycling is typical for the spinel electrodes under our experimental conditions, i.e. when the relative amount of the electrolyte is high compared to the mass of the spinel. Then side reactions become significant. Moreover, an additional layer, the so called solid electrolyte interphase (SEI), is expected to be formed on the spinel. This SEI is formed by the oxidation of the electrolyte solution. For the spinel films on p-doped silicon, only the electrolyte oxidation process is observed.

After the electrochemical cycling, partially cracked and peeled-off films are observed. The largest amount of "missing" film parts is observed on glassy carbon, which is possibly due to a lower adhesion between this substrate and the spinel film. The amount of the "missing" spinel film after cycling is highest on glassy carbon and lowest on p-doped silicon. As mentioned above, the as-grown $\text{Li}_{1+x}\text{Mn}_2\text{O}_{4-\delta}$ films show signs of compressive and tensile strain, respectively. The observed cracking and partial film removal after a number of electrochemical cycles can therefore be attributed to the inherent strain in the $\text{Li}_{1+x}\text{Mn}_2\text{O}_{4-\delta}$ thin films in conjunction with the periodic volume strain related to the removal and reloading of lithium ions during the electrochemical cycling.



Fig. 3. Typical cyclic voltammograms in 1 M LiClO₄/PC electrolyte at 0.05 mV s⁻¹of thin films of $Li_{1+x}Mn_2O_{4-\delta}$ on: (a) stainless steel and (b) glassy carbon. The thin films on p-doped silicon showed no electrochemical activity.

4. Conclusion

The comparison of the properties of thin $Li_{1+x}Mn_2O_{4-\delta}$ films with respect to the used substrate material (stainless steel, glassy carbon, and p-doped silicon) shows that there is a dependency on the substrate material with respect to the surface morphology, crystallinity, composition, and electrochemical properties of the resulting film. It is necessary, depending on the chosen substrate material, to use targets with different Li-stoichiometries to obtain the same final composition of the deposited film.

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