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Influence of metal layer coated glassy carbon substrates on the properties of PLD deposited $Li_{1+x}Mn_2O_{4-\delta}$ films

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$Li_{1+x}Mn_2O_{4-\delta}$ thin films were deposited on plain or coated (Au, Pt, Au/Pt) glassy carbon substrates using pulsed laser deposition. The aim of the coating was to improve the conductivity and the adhesion between film and substrate. The application of different intermediate layers influenced the crystallinity, the surface morphology, and the cycle stability of the spinel films. Films deposited on Au/Pt coated glassy carbon showed the most intense (111) orientation and the best defined surface morphology with tetrahedral and octahedral particle shapes. Compared to films on other metallic layer/glassy carbon combinations, $Li_{1+x}Mn_2O_{4-\delta}$ films on Au/Pt coated substrates displayed the lowest cycle stability.

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1. Introduction

Low weight rechargeable lithium-ion batteries are commonly used in portable devices or computing equipment. For such lithium-ion batteries $Li_{1+x}Mn_2O_{4.0}$ is a promising electrode material. Properties such as low toxicity, low material cost, and a comparatively high energy density in the potential range of 3.5 - 4.4 V vs. Li/Li^+ makes $Li_{1+x}Mn_2O_4$ attractive to be implemented as alternative electrode material for the commonly used $LiCoO_2$. A disadvantage of $Li_{1+x}Mn_2O_{4.0}$ is a charge capacity decrease during cycling. Possible explanations are a Jahn-Teller-distortion [1], solid electrolyte interphase (SEI) formation, and a possible dissolution of the manganese from the spinel [2]. To study the SEI formation a defined $Li_{1+x}Mn_2O_4$ electrode surface is required. Therefore it is necessary to use thin films with a defined surface instead of composite materials consisting of $Li_{1+x}Mn_2O_{4.0}$ powder and additives, to avoid a possible influence of the additives to a SEI formation. Thin films of $Li_{1+x}Mn_2O_{4-\delta}$ have been prepared by pulsed laser deposition (PLD) [3-7], radio frequency magnetron sputtering [8,9], electron beam evaporation [9,10], and electrostatic spray deposition (ESD) [11]. These films were deposited on various substrates such as silicon, stainless steel [5,6], platinum [12], glassy carbon [6], titanium [13], and gold [14,15]. Depending on the application, the appropriate substrate material is selected. For electrochemical studies, e.g., stainless steel, gold, and glassy carbon substrates are applicable due to their good conductivity and inertness during cycling. Titanium substrates are not suitable because of their electrochemical activity [13].

Metallic coatings on substrates are introduced to improve the adhesion between film and substrate, the conductivity, and the crystallinity of $Li_{1+x}Mn_2O_{4-\delta}$. In addition they can serve as a protection layer for the substrate itself. The aim of our study is to improve the $Li_{1+x}Mn_2O_{4-\delta}$ film properties by using different metallic coatings on glassy carbon and to increase the adhesion of $Li_{1+x}Mn_2O_{4-\delta}$ on glassy carbon [6].

2. Experimental

2.1 Film preparation and structural characterization

The used substrate was glassy carbon (GC; SIGRADUR G) as supplied by HTW, Thierhaupten, Germany. It was covered with an additional ≈ 10 nm thick metallic layer (Au, Pt, and Au(10 nm)/Pt(10 nm)) deposited by DC magnetron sputtering (TIPSI, 200 W (Au), 50 W (Pt), PK75 target, Argon, 0.3 Pa). The thin $Li_{1+x}Mn_2O_{4-\delta}$ films were deposited on these modified substrates using pulsed laser deposition (KrF excimer laser, repetition rate of 10 Hz, laser fluence 2.6 J cm^{-2}). During the deposition in 20 Pa oxygen the substrate, fixed at a target-substrate distance of 4 cm, was heated to 500 °C. After the deposition the films were cooled to room temperature within 30 min. The used rod like target was prepared by mixing $Li_{1.03}Mn_2O_4$ (99.7 % purity, Honeywell, Li/Mn = 0.515) with an excess of 2.5 Mol% Li_2O, pressing with 400 MPa, and sintering in oxygen for 10 h at 750 °C.

X-ray diffraction (XRD) measurements were performed between 12° and 85° at a scan rate of $0.014°min^{-1}$ (Siemens D-500 X-ray diffractometer, Cu K_α irradiation). The chemical composition was determined by using two analytical methods: Rutherford backscattering spectrometry (RBS, 2 MeV ^4He ions) for the Mn/O ratio and elastic recoil detection analysis (ERDA, $LiNbO_3$ standard, 12 MeV ^{127}I, incident angle 18°) for the Li/O ratio. The microstructure of the deposited films was investigated by high resolution scanning electron microscopy (SEM, SupraZeiss VP55), while the film thickness was obtained by profilometry (Dektak 8 profilometer).

2.2 Electrochemical characterization

The $Li_{1+x}Mn_2O_{4-\delta}$ films were electrochemically characterized in standard electrochemical cells at 25 (± 0.1) °C. The cells, which were assembled in a glovebox ($H_2O < 0.1$ ppm, $O_2 \sim 0.6$ ppm), consisted of the positive $Li_{1+x}Mn_2O_{4-\delta}$ working electrode on the respective substrate and the negative Li metal (Aldrich) counter electrode, separated by a 1 mm thick glass fiber separator. The used electrolyte was 1 M $LiClO_4$ in propylene carbonate (PC; Ferro, USA). Measurements were conducted in the potential range between 3.5 - 4.4 V vs. Li/Li^+. The electrode material was tested with cyclic voltammetry (0.05 mV s^{-1}) and galvanostatic charge/discharge ((1C-rate, 1C ≅ 13 µA cm^{-2}) experiments, using a computer-controlled celldata capture system (Astrol Electronic AG, Oberrohrdorf, Switzerland). After cycling the $Li_{1+x}Mn_2O_{4-\delta}$ films were washed with pure propylene carbonate and dried inside the glovebox. Subsequently, these films were characterized using scanning electron microscopy to study possible changes of the surface morphology.

3. Results and discussion

3.1 Film characterization: composition, crystallinity, and surface morphology

The average composition of the ≈ 300 nm thick films was $Li_{1.06}Mn_2O_{3.8}$. The films showed a lithium deficiency of 1.9 % and an oxygen deficiency of 5.7 % compared to the nominal target composition of $Li_{1.08}Mn_2O_{4.03}$. The relative error in film composition as determined with RBS and ERDA is 3-5 %. The lithium deficiency could be due to the noncongruent evaporation process during pulsed laser deposition, by scattering of lithium at heavier elements in the plume and background gas, or by sputtering/backscattering of the volatile lithium from the growing film [13,16]. The oxygen deficiency could be due to sputtering/backscattering from the growing films and/or a possible additional oxidation processes during the deposition, e.g., of the substrate material itself.

The measured XRD spectra (figure 1) correspond to the cubic $LiMn_2O_4$ spinel phase, and the crystallinity of these films improved using metallic intermediate layers. The most intense (111) reflexes were observed for films deposited on Au/Pt/GC (see Fig. 1). For all films, no impurities were detected.

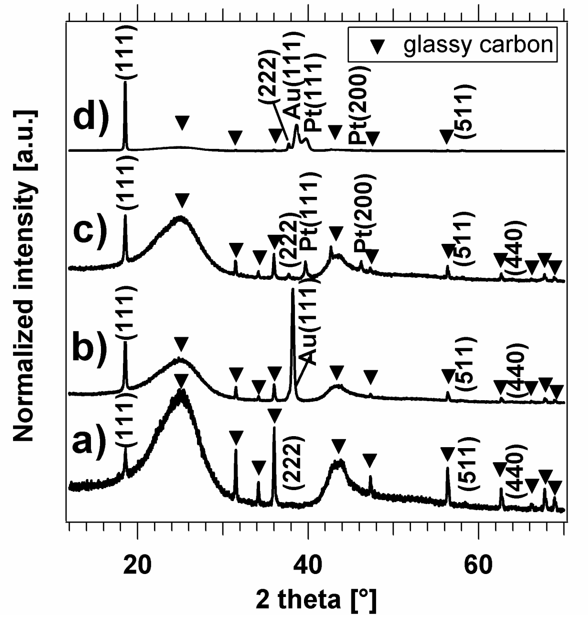
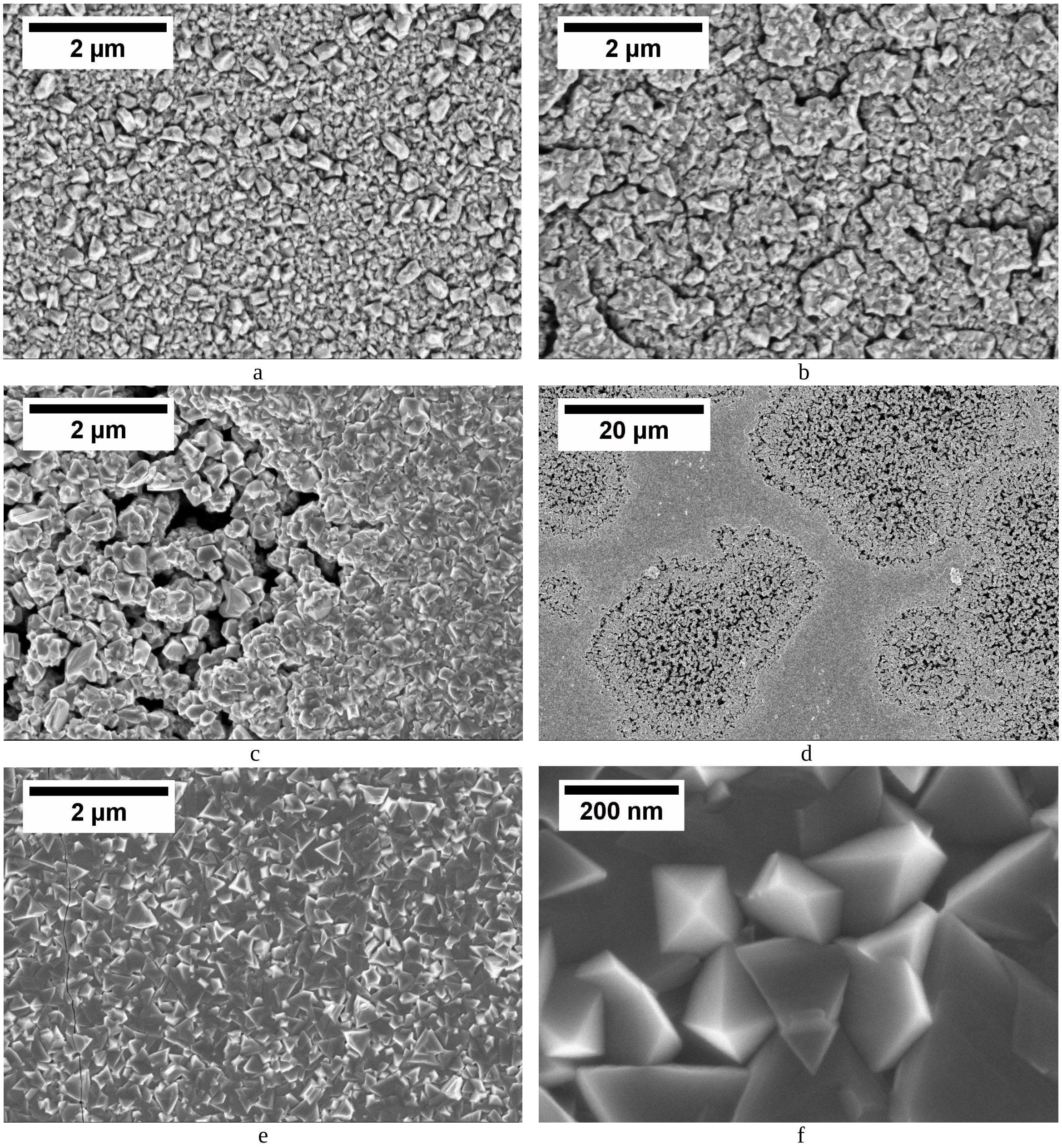


Fig. 1. X-ray diffraction patterns of $Li_{1+x}Mn_2O_{4-\delta}$ thin films (a) on glassy carbon, (b) on Au coated glassy carbon, (c) on Pt coated glassy carbon, and (d) on Au/Pt coated glassy carbon substrates. The reflexes of the glassy carbon are marked with ▼.

The use of Au and Pt intermediate layers resulted in a less uniform film surface morphology with areas of increased roughness (see figure 2 b-d); at the same time, regions lacking a close packing were observed. The reasons for the growth of a non-uniform spinel film on Au coated glassy carbon are possible morphological changes in the Au layer upon heating during growth. Furthermore it was observed that films deposited on plain or Au-coated glassy carbon had the lowest adhesion and in parts, these films peeled-off the substrate.



a b c d e f

Fig. 2. SEM images of thin $Li_{1+x}Mn_2O_{4-\delta}$ films deposited (a) on glassy carbon, (b) on Au coated glassy carbon, (c-d) on Pt coated glassy carbon, and (e-f) on Au/Pt coated glassy carbon substrates.

3.2 Electrochemical characterization of the thin films

During the charging process (oxidation) of the $Li_{1+x}Mn_2O_{4-\delta}$ thin film, lithium is de-intercalated in a two step-process thereby forming the nominal composition of MnO_2. Discharging (reducing) the electrode, lithium is re-intercalated thereby forming the nominal composition of $LiMn_2O_{4.0}$.

For all film-substrate combinations investigated the typical two oxidation/reduction peak pairs were observed. These agreed well with the redox peaks of the bulk $LiMn_2O_{4.0}$. A typical cyclic voltammogram of a $Li_{1+x}Mn_2O_{4-\delta}$ film deposited on uncoated glassy carbon substrate is shown in Fig. 3.

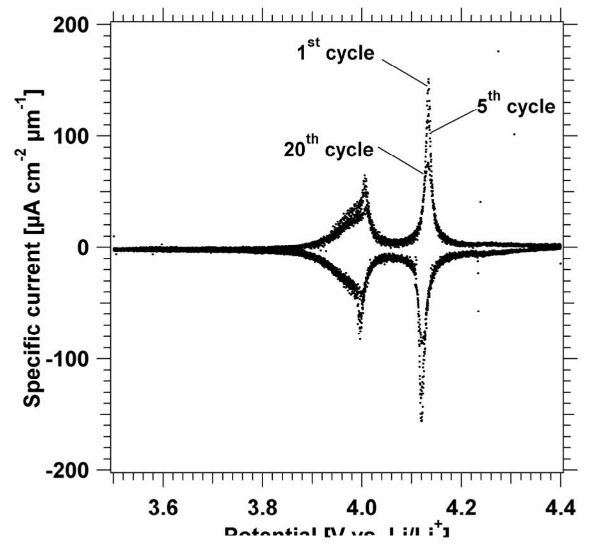
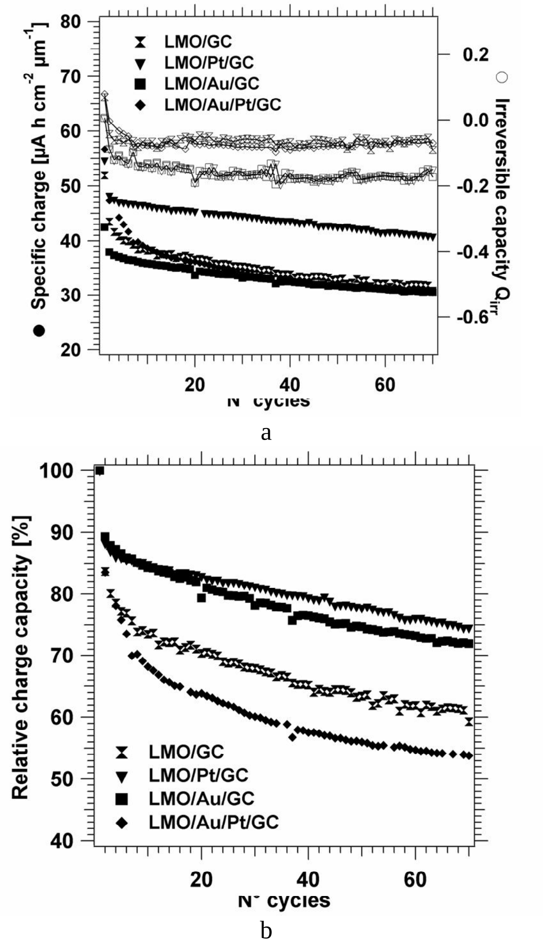


Fig. 3. Typical cyclic voltammogram in 1M $LiClO_4$/PC electrolyte at 0.05 mV s^{-1} of a $Li_{1+x}Mn_2O_{4-\delta}$ thin film deposited on uncoated glassy carbon.

The $Li_{1+x}Mn_2O_{4-\delta}$ films were tested with respect to their charging and discharging properties as well as charge cycle stability using galvanostatic charge/discharge techniques (1 C rate, potential limits 3.5 to 4.4 V). The ideal thin film model system should have a good substrate adhesion during cycling and good cycle stability. Therefore, the $Li_{1+x}Mn_2O_{4-\delta}$ thin films were studied with respect to changes of their charge capacity during cycling (specific charge, charge capacity decrease, irreversible charge) and changes of the surface morphology. The aim was to determine the best spinel/metal/GC combination to study the solid electrolyte interphase film formation.

The highest specific charges for the first cycle were obtained for $Li_{1+x}Mn_2O_{4-\delta}$/Au/Pt/GC (56.7 µA h cm^{-2} µm^{-1}) and $Li_{1+x}Mn_2O_{4-\delta}$/Pt/GC (54.7 µA h cm^{-2} µm^{-1}) and the lowest for films deposited on Au coated glassy carbon substrates (42.5 µA h cm^{-2} µm^{-1}) (see figure 4a). After 70 cycles the largest losses of the specific charge were noted for $Li_{1+x}Mn_2O_{4-\delta}$/Au/Pt/GC (46.2%) and $Li_{1+x}Mn_2O_{4-\delta}$/GC (40.7%), and the lowest for $Li_{1+x}Mn_2O_{4-\delta}$/Pt/GC (25.4 %) and $Li_{1+x}Mn_2O_{4-\delta}$/Au/GC (28 %), respectively (see figure 4b). The relative charge capacity is defined as C_x/C_1 * 100 (in %) (C_1 = specific charge after 1 cycle, C_x = specific charge after x cycles).



a

b

Fig. 4. (a) Specific charge (solid symbols) and irreversible charge capacities (open symbols) of the $Li_{1+x}Mn_2O_{4-\delta}$ films at the respective substrates for 1 C-rate (cf. Experimental part); (b) relative charge capacities of the $Li_{1+x}Mn_2O_{4-\delta}$ films deposited on glassy carbon, on Au coated glassy carbon, on Pt coated glassy carbon, and on Au/Pt coated glassy carbon substrates. The specific charges have been normalized with respect to the film thickness.

The cycling behaviour of the $Li_{1+x}Mn_2O_{4-\delta}$/Pt/GC showed an improved electrochemical performance by using Pt as an intermediate layer when compared to uncoated GC or GC coated with Au and Au/Pt. For all films the highest irreversible charge, defined as $Q_{irr} = (Q_C - Q_D)/Q_C$ where Q_C and Q_D are the respective charges for the charge (Li^+ extraction) and discharge (Li^+ insertion) steps, was determined during the first cycles (figure 4a). The negative irreversible capacity is due to the slightly higher discharge capacity than charge capacity in the respective cycle.

As already pointed out, $Li_{1+x}Mn_2O_{4-\delta}$ films deposited on Pt and Au coated glassy carbon had the highest cycle stabilities in contrast to films deposited on pure glassy carbon and Au/Pt coated glassy carbon substrates (see figure 4b). The decrease of the cycling stability can be affected by a loss in interfacial conductivity between the film and the substrate as a result of a reduced film-substrate adhesion. The best adhesion was observed for films on Pt coated glassy carbon. After cycling, these films were mainly intact. Films deposited on glassy carbon, on Au, and Au/Pt coated glassy carbon showed the lowest degree of adhesion. On Au/Pt/GC and pure GC, a high amount of film material peeled off the substrate. The decrease of charge capacity during the continuous cycling could be explained by a possible SEI formation as a result of an oxidative decomposition of the electrolyte and a gradually reduced adhesion between the $Li_{1+x}Mn_2O_{4-\delta}$ thin film and the substrate during cycling. Furthermore a possible dissolution of the manganese from the spinel [2] or an aging of the oxide electrode itself could also play a role.

4. Conclusions

The use of different metallic intermediate layers (Pt, Au, Au/Pt) results in a variation of the final $Li_{1+x}Mn_2O_{4-\delta}$ film properties compared to pure glassy carbon substrates. The additional metallic layer improved the crystallinity of the deposited spinel with a preferred (111) orientation, especially in the case of a Au/Pt intermediate layer. Only Pt intermediate layers lead to a stronger adhesion of the $Li_{1+x}Mn_2O_{4-\delta}$ thin films and a better electrochemical performance. In this case the lowest charge capacity decrease during cycling was obtained. Our experiments have shown that the $Li_{1+x}Mn_2O_{4-\delta}$/Au/Pt/GC combination is the best model electrode system to study a possible SEI formation because of the homogenous, well defined film surface morphology. Due to the reduced adhesion of $Li_{1+x}Mn_2O_{4-\delta}$ films on Au/Pt/GC, it is necessary to restrict the experiments to a smaller number of charge/discharge cycles, to ensure a mechanically intact $Li_{1+x}Mn_2O_{4-\delta}$ film.

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