Glassy carbon – A promising substrate material for pulsed laser deposition of thin Li$_{1+x}$Mn$_2$O$_{4-\delta}$ electrodes

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The spinel LiMn$_2$O$_4$ is a promising candidate for future battery applications. If used as a positive electrode in a battery, the charging capacity of such a battery element is limited by the formation of a solid electrolyte interphase (SEI)-like layer between the electrolyte and the spinel. To study the electrolyte–electrode interaction during electrochemical cycling, spinel thin films are deposited as model electrodes on glassy carbon substrates by pulsed laser ablation. The obtained polycrystalline oxide thin films show a well defined surface morphology and are electrochemically active. Adhesion of these thin films on glassy carbon is in general poor, but can be improved considerably by a surface pretreatment or adding a thin metallic coating to the substrate prior deposition. The best adhesion is obtained for films deposited on argon plasma pretreated as well as Pt coated glassy carbon substrates. During the electrochemical characterization of Li$_{1.06}$Mn$_{2.8}$O$_3$ thin film electrodes, no additional reactions of the substrate are observed independent of the used electrolyte. The best cycle stability is achieved for films on Pt coated glassy carbon substrates.

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1. Introduction

A major challenge for lithium-ion batteries with LiMn$_2$O$_4$ as positive electrode material is their capacity fading with increasing number of charging cycles. One reason is an increase of the spinels interface resistance due to a continuous formation of the so-called solid electrolyte interphase (SEI)-like layer on the oxide during charging and discharging. To understand the SEI formation processes at the positive electrode/electrolyte interface during the de-insertion (charging) and insertion (discharging) of lithium ions, it is advantageous to study electrodes without additional binder materials and conductive carbon, to exclude their suspected influence on the interface reactions. An established approach to prepare high quality thin films is the deposition of oxides by pulsed laser deposition (PLD). The deposition of the spinel LiMn$_2$O$_4$ by PLD on different substrates like silicon [1–5], titanium foil [1], indium tin oxide (ITO) [6], Pt [7,8], Au [8], glassy carbon (GC) [9,10] and stainless steel (SS) [3,11–13] has already been reported. However, several of these substrates are not suitable for an electrochemical characterization of electrode materials due to their own electrochemical reactivity in the potential range of interest to study the electrode material. Thus, to study the SEI formation in a model system, the use of electrochemically inert substrates is necessary. Previously, we reported the preparation of spinel thin films on stainless steel [13]. Thin spinel films deposited on this electrochemically inert substrate showed an inhomogeneous, non-reproducible surface morphology. Such films are not suitable for detailed electrochemical investigations of the electrode/electrolyte interface to study the SEI-like layer formation.

A substrate material of interest for thin film oxide electrodes is glassy carbon (GC), a material often used for electrochemical experiments. It is a non-graphitized carbon with a fullerene-related microstructure [14]. It has a high chemical stability, no open porosity and good electrical conductivity [15]. As shown in previous studies [9,10], GC is suitable for the deposition of LiMn$_2$O$_4$ thin films and their respective preparation as model electrodes for lithium-ion batteries. This paper summarizes our work performed to improve the structural properties of LiMn$_2$O$_4$ thin films deposited on non-modified and modified GC substrates. It also reflects on some electrochemical characterization done with respect to the spinel film properties.

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2. Experimental

2.1. Preparation of thin spinel films

Thin spinel films with a nominal composition of $\text{Li}_{1.03}\text{Mn}_2\text{O}_4$ were prepared by pulsed laser deposition (KrF excimer laser, repetition rate 10 Hz, $F=2.6\,\text{J}\,\text{cm}^{-2}$) on GC substrates (SIGRADUR G (GC G) and SIGRADUR K (GC K), from HTW Hochtemperaturwerkstoffe, Thierhaupten, Germany). GC K, prepared at higher temperatures than GC G, has a higher conductivity and a lower reactivity to oxidizing species than GC K. The GC G substrates were used as delivered and with differently treated surfaces: Some GC G substrates were polished with an aqueous diamond paste solution (3 μm particle size) for 10 min (GC G, polished), washed with methanol and de-ionized water in an ultrasonic bath with a subsequent dried step using N₂ [16]. Other GC G substrate surfaces were treated in an argon plasma (GC G, argon) with a RF power density of 0.57 W cm$^{-2}$ at ≈ 120 mbar. Furthermore, GC G substrates were coated with an additional ≈ 10 nm thick metallic layer (Au, Pt, or Au (10 nm)/Pt (10 nm)) deposited by DC magnetron sputtering (GC G, metal, 200 W (Au), 50 W (Pt), PK75 target, $p_{\text{Ar}}=0.003$ mbar).

For the spinel deposition the substrate–target distance was fixed at 4 cm. The samples were kept during the deposition at 500 °C in an oxygen background pressure of 0.2 mbar. After the deposition, the films were cooled within 30 min to room temperature. The cylindrical target was prepared by mixing $\text{Li}_{1.03}\text{Mn}_2\text{O}_4$ (99.7% purity, Honeywell, Li/Mn = 0.515) with an excess of 2.5 Mol% Li$_2$O (99.5% purity, Alfa Aesar) pressing with 400 MPa, and sintering in oxygen for 10 h at 750 °C. The final target composition was $\text{Li}_{1.08}\text{Mn}_2\text{O}_4$ in order to compensate the Li-loss during the ablation process.

2.2. Preparation of a classical spinel composite electrode

As a reference, spinel composite electrodes were prepared by mixing 80 wt% of $\text{Li}_{1.03}\text{Mn}_2\text{O}_4$ (99.7% purity, Honeywell, Li/Mn = 0.515) as the active material, 10 wt% Carbon black (Super P, TIMCAL SA) as conductive additive, and 10 wt.% polyvinylidene fluoride binder (PVDF SOLEF 1015, Solvay) dissolved in N-methylpyrrolidinone (NMP, Fluka). The slurry was spread by doctor blading on aluminium foils and then dried in air at 80 °C. Afterwards the dried electrodes were blanked out (electrode area 2.3 cm$^2$). The weight of the active material was in the range 2.8–3.5 mg for each sample.

2.3. Characterization of the spinel electrodes

The spinel thin films were characterized after the deposition with respect to their composition, crystallinity, surface morphology before and after charging/discharging, thickness and electrochemical properties using standard electrochemical instrumentation. The composition was determined by Rutherford backscattering (RBS, 2 MeV $^4$He ions) and elastic recoil detection analysis (ERDA, 12 MeV $^{12}$C, incident angle 18°, LiNbO$_3$ standard) and the crystallinity by X-ray diffraction (Siemens D-500). To characterize the surface scanning electron microscopy has been employed (SupraZeiss VP55, InLens and SE2 detector, 3 kV) while the thickness was measured by a Dektak 8 profilometer.
For the electrochemical characterization at 25 (±0.1) °C, the spinel films were used as positive electrodes in coin-type model electrochemical cells separated with a glass fiber separator from a lithium electrode (Aldrich) which also serves as reference electrode. The following electrolytes were used: 1 M LiPF6 in EC/DMC (1:1) (EC: ethylene carbonate, DMC: dimethyl carbonate; Ferro), 1 M LiClO4 in PC (PC: propylene carbonate, Ferro) and 1 M LiClO4 (Aldrich, 99.9%) in DMC (Merck). After assembling the cells in an argon filled glove-box (H2O < 0.1 ppm, O2 about 0.6 ppm, 25 (±0.1) °C) the spinel films and composite electrodes were electrochemically analyzed by cyclic voltammetry (sweep rate 0.05 mV s⁻¹, 20 cycles) and galvanostatic charge/discharge (1C-rate, 1C ∼= 13 μA cm⁻²) experiments between 3.5 V and 4.4 V vs. Li/Li⁺, using a computer-controlled celldata capture system (Astrol Electronic AG, Oberrohrdorf, Switzerland).

After cycling the electrodes were washed in pure organic solvents (DMC or PC) and dried at room temperature in the glove box. The films were characterized afterwards with respect to their surface morphology.

3. Results and discussion

3.1 Li1+xMn2O4.8 on glassy carbon substrates

The average composition of ≈300 nm thick spinel films was determined by RBS and ERDA with a calculated composition of Li1.06Mn2O3.8 with an experimental uncertainty of typically ±3% for Li and ±5% for oxygen. A lithium deficiency of 1.9% as compared to the nominal target composition of Li1.08Mn2O4.03 and an oxygen deficiency of 5.7% were noted. The lithium deficiency origi-
nates from a non-congruent lithium transfer as a result of scattering processes with heavier species in the plasma plume and the background gas. In addition, there are backscattering processes at the surface of the growing film by the incoming species [17–19]. Likewise, an oxygen deficiency in these oxides can originate as a result of backscattering and/or sputtering processes of oxygen at the film surface. Often, an in situ oxygen annealing step at atmospheric pressure is introduced for many oxides grown at similar conditions to compensate the oxygen loss. This annealing step has been omitted because LiO₂ can form during the annealing step which will reduce the Li content in the spinel.

X-ray diffraction pattern of spinel thin films grown on differently treated GC are presented in Fig. 1a and b. The X-ray intensities of the polycrystalline thin films correspond to the cubic LiMn₂O₄ spinel [11,17]. Compared to the powder material the lattice constant of the thin film is shifted from the expected value of 8.248 Å [20] to 8.267 Å which is suggestive of compressive strain in these films.

A classical electrode consists typically of ≈120 nm sized carbon black and μm sized Li₁.₀₃Mn₂O₄ particles, mixed with the PVDF binder. The roughness of these electrodes is very high, typically in the μm-range. A better homogeneity and a reduced roughness (∼20–40 nm) can be achieved by growing the spinel as thin film. Films show a regular surface morphology as shown in Fig. 1b, which is better suited for the electrochemical characterization. It is noted, that a low adhesion of the Li₁.₀₆Mn₂O₃.₈ thin films on GC substrates is observed, which results in some cases in a spontaneous peeling-off of the film. A low adhesion is likely be related to the compressive

![Figure 3](image-url)

**Fig. 3.** (a)–(d) Typical cyclic voltammograms (0.05 mV s⁻¹) of (a) classical spinel electrodes (1st cycle; used electrolyte: 1 M LiPF₆ in EC/DMC in black, 1 M LiClO₄ in DMC in dark grey, 1 M LiClO₄ in PC in grey); and of Li₁+xMn₂O₄−₁ films deposited on uncoated glassy carbon substrates (b)–(d): with the following electrolytes: (b) 1 M LiPF₆ in EC/DMC, (c) 1 M LiClO₄ in DMC, and (d) 1 M LiClO₄ in PC.

![Figure 4](image-url)

**Fig. 4.** Specific charge/discharge (not connected symbols) and irreversible capacities (connected symbols) of the spinel electrode for a 1 C-rate cycled in 1 M LiClO₄ in PC at 3.5–4.4 V vs. Li/Li⁺. The specific charges and discharges have been normalized with respect to the film thickness. The square symbol mark the obtained data for the thin model electrodes while triangle symbols are used for the data of the classical composite electrode.
stress in these films and the resulting removal of the electrode has been identified as one of the most important origins of the fast capacity fading of the thin film electrodes.

To obtain a better substrate-film adhesion, the substrate surface prior deposition can be modified with methods such as plasma cleaning, polishing or to coat the surface with a very thin metal layer. For GC, there is also the possibility to use different types of GC like GC\textsubscript{C} and GC\textsubscript{K}. For films grown on plain and polished GC\textsubscript{C} and GC\textsubscript{K} or plasma cleaned surfaces, no changes in the crystallinity or the presence of impurities were observed by X-ray diffraction. In the case of polished GC no significant improvement of the film adhesion was obtained, whereas for spinel films grown on plasma cleaned surfaces the adhesion improves significantly. The surface morphology of an argon treated uncoated GC\textsubscript{C} substrate changes dramatically with the formation of a regular array of cone-shaped features (average height \( \approx 200-250 \text{ nm} \)) thereby increasing the sur-
face roughness considerably (Fig. 1c). This surface modification is the likely reasons for an improved adhesion together with a chemically modified surface [16] (e.g. formation of C–OH groups). The use of GCK does not significantly improved adhesion.

Thin metal coatings on GC substrates are another route to improve adhesion of Li1+xMn2O4 films. The application of different metallic intermediate layers (Pt, Au, Au/Pt) results in changes of the Li1.06Mn2O3.8 film properties compared to films on pure glassy carbon substrates. A detailed description and analysis of the spinel deposition by PVD of the metal coated GC is presented elsewhere [9]. X-ray diffraction patterns of spinel films deposited on metal-coated glassy carbon are shown in Fig. 1b. The additional metallic layer improves the crystallinity of the deposited spinel with a preferred (1 1 1) orientation, in particular for GC with a Au/Pt layer. It is interesting to note, that the surface morphology of these films also depends on the applied intermediate metallic layer.

Films deposited on Au or Pt coated substrates are porous and show an irregular surface morphology (see Fig. 2b–d). A very homogeneous surface morphology is obtained for Li1+xMn2O4 films on GC Au/Pt (Fig. 2e, and f), where symmetrical octahedral and tetrahedral particles are present. The relatively smooth surface morphology of Li1+xMn2O4 on GC Au/Pt is well suited to serve as a model electrode to study the SEI-like layer formation. However, it can be expected that electrochemical studies are limited to a few charging/discharging cycles due to the in low general adhesion of Li1+xMn2O4 on GC Au/Pt.

3.2. Electrochemical properties of Li1+xMn2O4 films on glassy carbon substrates

The spinel electrodes were electrochemically tested with different electrolytes between 3.5 V and 4.4 V vs. Li/Li+ to determine possible differences between the classical composite and the model electrodes. The corresponding cyclic voltammograms for the composite and thin films are shown in Fig. 3a and b–d, respectively. Here the typical oxidation and reduction behaviour of the spinel was observed for thin film and composite electrodes [21]. Lithium ions are extracted from the electrodes in two reversible steps from the spinel and α-MnO2 is formed during charging (oxidation process) [5,12]. During the discharging (reduction) process lithium ions are re-inserted. The cyclic voltammograms of the composite electrode are presented in Fig. 3a. A small shift of the redox potential pairs is observed in Fig. 3a depending on the used electrolyte. This could be the result of kinetic effects, e.g. caused by the different diffusion of the lithium ions in the spinel or in the porous electrode itself [22]. In the case of 1 M LiClO4 in DMC for the classical electrode an additional oxidation reaction is detected also observed for thin spinel films (see Fig. 3c).

The DMC is probably decomposed by oxidation and a SEI-like layer is formed. Thin films and the composite electrodes show in general a good cycling performance for 1 M LiPF6 in EC/DMC (1:1) and 1 M LiClO4 in PC. Broader peaks in the cyclic voltammogram are observed for the composite electrodes as compared to the film electrodes. This is due to the larger particles size of the spinel in the electrode. The cyclic voltammogram of the untreated glassy carbon in 1 M LiPF6 in EC/DMC and in 1 M LiClO4 in PC reveals also an oxidation reaction but with low intensity (not shown). In the case of the spinel covered glassy carbon substrates this additional reaction was not detected. Compared to the 1 M LiPF6 in EC/DMC electrolyte a higher cycling stability, i.e. a smaller charge decrease during cycling, is observed for 1 M LiClO4 in PC as electrolyte. The obtained decrease of the capacity is probably due to the formation of the SEI-like layer or an aging of the electrode.

Spinel electrodes were also galvanostatically characterized (1C-Rate, 1C = 13 μA cm–2). The specific charge capacities and the irreversible capacities for the cycling of the composite electrode and the model electrode are presented in Fig. 4. The specific charges are normalized with respect to the film thickness. The highest amount of irreversible capacity for both kinds of electrodes is obtained after the first cycle. The charge capacity loss between the first and the second cycle is about 3% for the classical electrode and 7–16% for the model electrode. After 10 cycles the charge decrease is more significant for the model electrodes (13–27%) than for the classical electrodes (about 6%). Analysing the thin film electrodes by SEM shows that a high amount of material is removed i.e. holes in the spinel films, which explains the pronounced capacity decrease during cycling compared to classical electrodes. The better cycling stability of the classical electrodes can be explained by the additive carbon black in the electrode. It is known from the literature, that additives like carbon black improve the conductivity in the electrode [23,24].

The highest charge capacity for the first cycle is obtained for films grown on GC treated with an argon plasma (Fig. 5a). Likewise, the decrease of charge capacity is significantly larger than for the other film-substrate combinations (non- and pre-treated). As a result, the highest irreversible capacity is obtained (Fig. 5b). The best adhesion with respect to charging and discharging cycles is noted for films on GC argon, where the films remain intact after cycling. SEM images of two cycled electrodes are presented in Fig. 5c and d. On both surfaces, an additional layer on the electrode surface is clearly visible. It is a layer formed during cycling which is associated with the SEI-like layer. This newly formed layer seems to be very thin and difficult to detect because the layer is embedded between the larger particles (see white arrows) and only noticeable on smoother films.

For all systems tested with Pt intermediate layers an improved adhesion of the Li1.06Mn2O3.8 thin films as compared to untreated GC substrates is obtained. The adhesion after cycling of the Li1+xMn2O4/GC is similar to the spinel films on GC argon. The specific charge capacity and irreversible charge capacities of Li1+xMn2O4 films on the respective substrates, which were cycled with a 1 C-rate, are presented in Fig. 5e and f, respectively. The lowest charge capacity decrease during cycling is obtained for films deposited on Pt coated substrates. The calculation of the relative charge capacity (Ct/C0 × 100 (in %)) (Ct = specific charge after 1 cycle, C0 = specific charge after x cycles) reveals, that after 70 cycles the largest losses of the specific charge are obtained for Li1+xMn2O4/GC Au/Pt (46.2%) and Li1+xMn2O4/GC (40.7%), while the lowest losses are observed for Li1+xMn2O4/GC Au (25.4%) and Li1+xMn2O4/GC (28%). The large loss of charge capacity is mainly due to the low adhesion, the loss of electrical contact during cycling, and/or material aging. Overall, a spinel deposited on Pt coated GC gives the best results with respect to mechanical properties like adhesion and electrochemical performance.

4. Conclusion

Glassy carbon is a good conductive substrate material for thin Li1+xMn2O4 electrodes. The films obtained by pulsed laser deposition reveal a well defined surface morphology and the typical spinel activity during electrochemical cycling. No additional reactions (oxidation or reduction) of the substrate material are observed during cycling. The deposited thin films show a good cycling behaviour in different electrolytes compared to classical spinel composite electrodes, but the adhesion of the thin films is relatively low. Different approaches have been tested to improve the adhesion of the thin films i.e. by polishing, argon ion plasma etching, by coating with a metallic layer or by applying a different type of GC. The best adhesion and cycling stability was obtained for films, deposited on argon plasma etched GC and Pt coated GC substrates.
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