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# The influence of preparation conditions on structural evolution and electrochemical properties of sputtered $LiNi_{0.5}Mn_{1.5}O_4$ thin film electrodes

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ABSTRACT

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) thin films were prepared by radio frequency magnetron sputtering, followed by thermal annealing in ambient atmosphere. The growth of the films has been studied as a function of deposition temperature, atmosphere, and annealing temperature. Electrochemical properties of LNMO thin-film cathodes were investigated using galvanostatic charge/discharge and cyclic voltammetry against a lithium anode. The initial capacity and capacity retention of the films are highly dependent on the crystallinity and morphology of the films. LNMO thin film grown at 400 °C in an $Ar/O_2$ atmosphere and annealed at 550 °C exhibits good crystallinity and well-defined grain structure. Also it exhibits larger capacity and higher cyclic stability under a high cutoff voltage of 4.9 V.



## 1. Introduction

The spinel $LiNi_{0.5}Mn_{1.5}O_4$(LNMO)was expected to meet the high energy and power demands of electric equipment for a possible replacement of standard $LiCoO_2$, $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ and $LiFePO_4$ cathodes [1–3]. It has a reaction voltage near 4.7 V and a high theoretical gravimetric capacity of 147 mAh/g and a large weight energy density [4,5]. Also, it is one of the few cathodes to pair up with high working voltage anodes, such as $Li_4Ti_5O_{12}$, to construct batteries with very high power capabilities [6], which lead to less sacrifice in energy density. The operation at high voltages of LNMO thin-film stems from the oxidation of Ni ions, and the structural stability can be kept because of Mn ions [7]. Moreover, spinel LNMO cathodes have a relatively high rate capability because of the 3D diffusion pathways for $Li^+$ ions. Thus, it is one of the most attractive cathodes for the next generation advanced lithium ion batteries.

Thin film electrodes have been proposed as an ideal model system to clarify the electrochemical reactions that occur at the electrode surface [8–10]. First, thin film electrodes free of binder and conductive additive can be employed to understand the electrochemical activities of pure active materials. Then, thin films provide a flat electrode surface, and the thickness has been reduced to a value at which the transport and diffusion of electrons and ions can take place instantly, so thin film electrodes can naturally suppress the intrinsic drawbacks. Third, anisotropic reactions dependent on the crystal orientation can be detected. Moreover, thin film electrode can be utilized in all-solid-state thin film batteries, which have a range of prospective applications, such as non-volatile memories, remote sensors, and smart cards. Studies on thin film electrodes have been mainly applied to $LiCoO_2$ and $LiMn_2O_4$, and there have been limited reports of preparation and subsequent electrochemical investigations on thin-film LNMO cathodes [11–13].

In order to grasp a better insight in the relationship between the LNMO films preparation process and their electrochemical properties, and to further understand the origin of the capacity decreasing over cycles, we report the growth of LNMO thin films using radio frequency magnetron sputtering, followed by thermal annealing. The structure, crystallinity, orientation and surface morphology of the films were characterized, and their corresponding charge/discharge behavior, cyclic voltammetry (CV), and cycle stability of the samples were also investigated.

## 2. Experimental

The LNMO target was prepared by the conventional solid state reaction of $Li_2CO_3$, NiO and $MnO_2$, and the powders were thoroughly mixed, pelletized, and calcinated at 1000 °C for 12 h to obtain appropriate amount of lithium excess LNMO targets.

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The LNMO thin films were deposited on stainless steels (SS) and $SiO_2$/Si (SOS) substrates by magnetron sputtering at a base pressure $\sim 8 \times 10^{-5}$ Pa for 2 h. Deposition temperatures were set as room temperature and 400 °C, respectively. The deposition pressure is always controlled to 1.2 Pa. When varying the deposition atmosphere by oxygen ventilation, $Ar/O_2$ ratio is set as 4:1. The annealing process was conducted at 350–550 °C for 2 h in a tube furnace with a heating rate of 5 °C/min. Following annealing, the samples were furnace-cooled to room temperature. The loading of the thin-film electrode was obtained ~0.3 mg by weighing the substrate before and after film deposition, and the measured mass have a fluctuation of ±6%.

Surface morphology and compositions of LNMO thin films on SOS substrates were characterized by field emission scanning electron microscopy (FESEM) and Energy Dispersive Spectrometer (EDS). The crystallinity characterization and electrochemical measurements were performed on the films on SS substrates. The Grazing Incidence X-ray Diffraction (GIXD) of thin-films was collected to characterize crystallinity in the range of 15–80° at a scan rate of 4°/min.

Charge–discharge measurements were examined using 2032-type coin cells assembled in an argon-filled glove box with lithium metal as the counter electrode. A LNMO thin film of approximately 1.766 $cm^2$ of active area as the working electrode, and 1 mol/L $LiPF_6$ in a 1:1 solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte, and a thin sheet of microporous polyethylene (Celgard 2400) was served as the separator. For the charge–discharge tests, the cells were charged to 4.9 V and discharged to 3.2 V at a current density of 10 μA (5.66 μA/$cm^2$). CV measurements were carried out in the voltage range between 3.2 and 4.9 V with a scan rate of 0.2 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range between 1 MHz and 0.01 Hz.

## 3. Results & discussion

### 3.1. Surface morphology and crystallinity

Fig. 1 shows the SEM images of the films deposited at different substrate temperatures and atmosphere. The thickness of thin-film is measured with ~500 nm. All films deposited exhibit a relatively smooth surface without big particles or droplets on the surfaces. At RT and Ar atmosphere, the surface of LNMO thin film is composed of flake-like small and discrete particles between them. The film underneath these particles exhibits a nearly amorphous nature, without any obvious grains can be observed (Fig. 1a). At 400 °C and Ar atmosphere, the amount of the discrete particles on the top of the film is reduced (Fig. 1c). This is because the high substrate temperature lead to the high atom mobility, therefore, atoms are not easy to cluster to form discrete particles. At RT and $Ar/O_2$ atmosphere, the film has some cracks and shows informity (Fig. 1b). By increasing the deposition temperature, the film shown in Fig. 1d is composed of small grains (<100 nm), and no more an amorphous morphology, so the oxygen ventilation result in better crystallization. It can be seen that the deposition parameters played an important role on morphology evolution [14,15].

Fig. 2 shows the SEM images of the sputtered LNMO films (Fig. 1a, c, and d) annealed at different temperatures from 350 to 550 °C for 2 h. The sample in Fig. 1b with some cracks was ruled out. After annealing at 350 °C, the film deposited in RT and Ar atmosphere is composed of small grains with an average grain size of ~100 nm. The films appear very dense, and grains are not well defined, as shown in Fig. 2a. As the annealing temperature ($T_A$) increases to 450 °C, the morphology of the LNMO thin film displays no considerable difference in sizes and shapes. When annealed at 550 °C, the structure with better defined grain boundaries (Fig. 2c) can be obtained, indicating an improved crystallinity (Fig. 2d–f). These morphology changes are similar to the films deposited at 400 °C and Ar atmosphere. As for the films deposited at 400 °C and $Ar/O_2$ atmosphere, the grains are well defined, and the average grain size also increases with increment of temperature. When annealed at 550 °C, the LNMO thin film exhibits a more dramatic change in morphology. The well-defined grains are in the range between 200 and 300 nm. The grain shape reflects the spinel structure, a high proportion of pseudo-polyhedral or triangle with better defined edges and faces. Moreover, the EDX analysis reveals the Mn/Ni ratios of the films between 2.3 and 2.7, which are in close agreement with the expected value of three and comparable to the previous reports. However, the ratio of O and Li might be varied because of different annealing temperatures and atmosphere. The high temperature and oxygen atmosphere increase the atom mobility, reduce surface energy of the film and therefore improve the crystallinity.

### 3.2. Structure characterization

When Mn is substituted by Ni atom in spinel $LiMn_2O_4$, the structure of LNMO is no longer a typical spinel. In the ordered phase of the LNMO, the Li atoms occupy 8c sites, Ni atoms and Mn atoms are located at the 4a and 12d sites, and O atoms inhabit the 8c and 24e sites (space group of $P4_332$). When oxygen deficiency exists in the LNMO structure, which introduces $Mn^{3+}$ and disorder into the spinel phase, and some of the grains may crystallize into a disordered phase in order to maintain the valence state, where Li atoms are located at the 8a sites, Mn and Ni atoms are randomly distributed at the 16d sites, and O atoms occupy the 32e sites (space group of Fdm) [16]. Moreover, the disordered phase has better electrochemical performance.

The microstructure and crystallinity of LNMO thin films are dependent on deposition temperature, atmosphere, and annealing temperature. Fig. 3 shows the XRD spectra obtained from films (Fig. 1a, b, and d) annealed at different temperatures ranging from 350 to 550 °C. All peaks are matching to spinel phase with space group Fdm (PDF 80-2162), suggesting that the post annealed LNMO films are polycrystalline and composed of fine grains.

When the films are deposited at the RT and 400 °C in Ar atmosphere, the amorphous structure was indicating that the films were not well crystallized. After annealing, their XRD spectras are shown in Fig. 3a. As for the films deposited in RT, with increase in the annealing temperature, the intensity of (111), (311) and (400) peak increases. Meanwhile, two tiny peaks (511) and (400) are observed. At $T_A$ 550 °C, a (400) texture develops. For the annealed film deposited at 400 °C with Ar atmosphere. With the increased annealing temperature, the intensity of (311) peak develops, while that of (400) peak is reduced. One major peak from (400) diffraction is observed of films annealed at 350 °C, and a (311) texture develops when annealed at 550 °C. Also, some XRD spectrum shows a very weak diffraction peak of (511) and (440). For films deposited at 400 °C and $Ar/O_2$ atmosphere, the (111) peak presents highest at $T_A$ 550 °C, minor peaks of (400) also observed in the spectra. Moreover, (311) peak appears in the film at $T_A$ 550 °C, indicating good crystallinity. Two minor peaks of impurity phases marked as * exist in some spectra. The impurities such as NiO and $Li_xNi_{1-x}O$ were often observed in the final product after high temperature synthesis. Therefore, the substrate temperature and oxygen atmosphere are two important factors which can significantly affects the microstructure of films. The $O_2$ atmosphere also improves the crystallinity of the film, and its effect on the film crystallinity is more obvious than the substrate temperature effect.