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High power and capacity of $LiNi_{0.5}Mn_{1.5}O_4$ thin films cathodes prepared by pulsed laser deposition

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ABSTRACT

Lithium secondary batteries using $LiNi_{0.5}Mn_{1.5}O_4$ films as a cathode material were prepared by pulsed laser deposition on stainless steel substrates. X-ray diffraction and Field-emission Scanning Electron Microscope results show that the film deposited at 750 °C exhibits good crystallinity with well-defined grains structure. Charge/discharge behavior of the batteries under a high cutoff voltage of 4.9 V vs. Li was highly improved by using Li-rich samples, which exhibits larger specific capacity and higher rate capability. Especially, when the substrate temperature increases to 750 °C, the reversible capacity maintains 116.8 mAh g^{-1} after 100 cycles at 0.5C, and the Coulombic efficiency is almost a constant value of 98%. It also exhibits excellent rate capability, as the rates increase to 5 and 10C, and about 95.4% and 92.3% of its initial capacity at 0.2C can be retained.

1. Introduction

Nowadays, Li-ion batteries are widely used in portable electronic devices such as mobile phones, laptop computers and camcorders. It is known that the performance and the utilization of batteries are mainly limited by the properties of cathode materials, which determine the capacity, stability, conductivity and safety. Among various cathode materials, spinel $LiMn_2O_4$ was extensively investigated due to its economical and environmental advantages. However, the main drawback of spinel $LiMn_2O_4$ lies in its irreversible capacity loss during storage and cycling, which is due to the Jahn–Teller effect, structural instability at high potentials or to manganese dissolution. To further improve the quality, one effective method is to replace Mn by other transition metals to obtain $LiM_xMn_{2-x}O_4$ (M = Co [1], Al [2], Fe [3], Ni [4], Cr [5], etc.). Among these doping approaches, $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) spinel is considered as an attractive candidate because of its many excellent electrochemical properties, such as large specific capacity close to the theoretical value 146.6 mAh g^{-1}, high working voltage 4.8 V, and high charge/discharge rate capability [6,7]. Recently, Zhou et al. [8] reported that LNMO hollow microspheres/microcubes delivered a discharge capacity of about 120 mAh g^{-1}, corresponding to 96.6% of the initial capacity after 200 cycles at 2C. Xiao et al. [9] synthesized Cr-substituted LNMO composite particles to control the concentration of Mn^{3+} ions in the lattice, which showed about 120 and 100 mAh g^{-1} at 5 and 10C, respectively.

In order to obtain high-quality LNMO film batteries, some methods, including electrophoretic deposition [10], spin-coating [11], and pulsed laser deposition (PLD) [12], have been used. Among them, PLD technique shows many advantages, for example, high deposition rate, good crystallinity, easy to control thickness and uniformity, and direct stoichiometry transfer from the target to the film. In fact, some thin-film cathode materials with good performance have been fabricated by this method. Simmen et al. [13] reported $Li_xMn_2O_4$ films grown on stainless steel (SS) substrates exhibiting about 75% of the capacity, when the current density increases from 1 to 16C. Xia et al. [14] found the initial capacity of LNMO films can be as high as 122.5 mAh g^{-1} with a constant current of 20 μA/cm^2, and 96% of the initial capacity can be retained after 50 cycles. Normally, SS is used as substrate to grow thin film electrodes due to its stability against the liquid electrolyte and low cost. However, in some cases, the iron on surface of the substrate can more easily diffuse into the films with increasing deposited temperature and form various electrochemically inactive oxides, which suppress the migration and diffusion of lithium ions in charge and discharge [23]. Therefore, it is urgently necessary to find an effective method

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to improve the electrochemical properties of the film grown on SS substrate by PLD technique.

In this work, we report the growth of Li-rich LNMO thin films on SS substrates using PLD technique at different temperature. The structure, crystallinity, orientation and surface morphology of the films were characterized. Charge/discharge behavior, cycle performance, and rate capability of the samples were also investigated. It is found that the Li-rich sample grown and annealed at 750 °C exhibits higher cycle stability and specific capacity, especially at high rate measurement.

2. Experimental

The LNMO thin films were deposited on SS and SiO_2/Si (SOS) substrates by PLD in a vacuum chamber at a base pressure less than 10^{-3} Pa. The target was prepared by the conventional solid state reaction method. The original materials, MnO_2 99.9%, NiO 99.9%, LiOH 99.9%, were mixed using ball mill for 8 h. The mixtures were placed in corundum crucible, and heat-treated in air at 750 °C for 20 h. It was then ground, mixed, pelletized and calcined in air at 1000 °C for 12 h to obtain appropriate amount of lithium excess LNMO targets. A KrF (Lambda Physik, 248 nm) laser beam was used as the laser source with the energy density at the target surface of 2 J/cm^2 and the repetition frequency of 10 Hz. Before the deposition, the chamber was vacuumed to the base pressure and then introduced the high-purity oxygen to keep the pressure of 26 Pa. Films depositions were carried out at different temperatures ranging from 550 to 750 °C. The deposition time was 60 min, followed by 1 h in situ annealing at the same condition.

The structure and cystallinity of the films were investigated by X-ray diffraction (XRD, PANalytical B.V.) with Cu Kα radiation (λ = 1.5406 Å). The diffraction patterns of the products were taken in the 2θ range from 10° to 70° at a step model with a step size of 0.02°. The surface morphologies of thin films were characterized using Field-emission Scanning Electron Microscope (FSEM, Sirion 200, Holland). LNMO films with different excess of lithium ions, which were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, ELAN DRC-e, Perkin Elemer), were selected as cathodes. The chemical valence states of Mn, Ni and Fe on the surface of the samples were investigated using X-ray photoelectron spectroscopy (XPS, Perkin-Elmer, PHI 5600) with a monochromatic Al X-ray source (1486.6 eV). The data were calibrated using adventitious C 1s peak with a fixed value of 284.4 eV and analyzed using

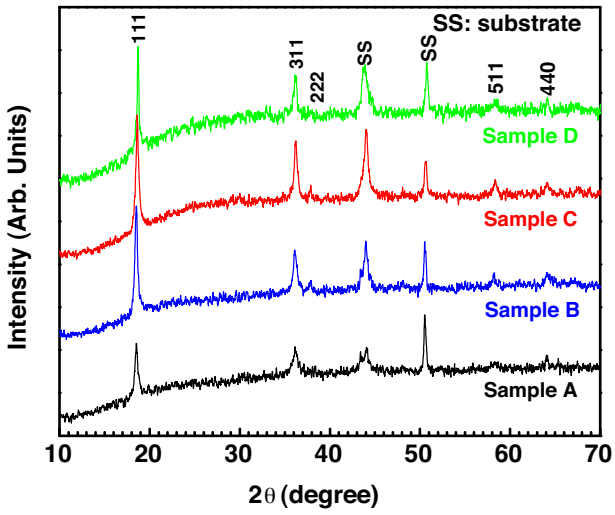

Fig. 1. XRD spectrum of the Li-rich LNMO films deposited at different temperatures, (550 (Sample A), 650 (Sample B), 750 °C (Sample C)), and Sample D at 750 °C as a reference.

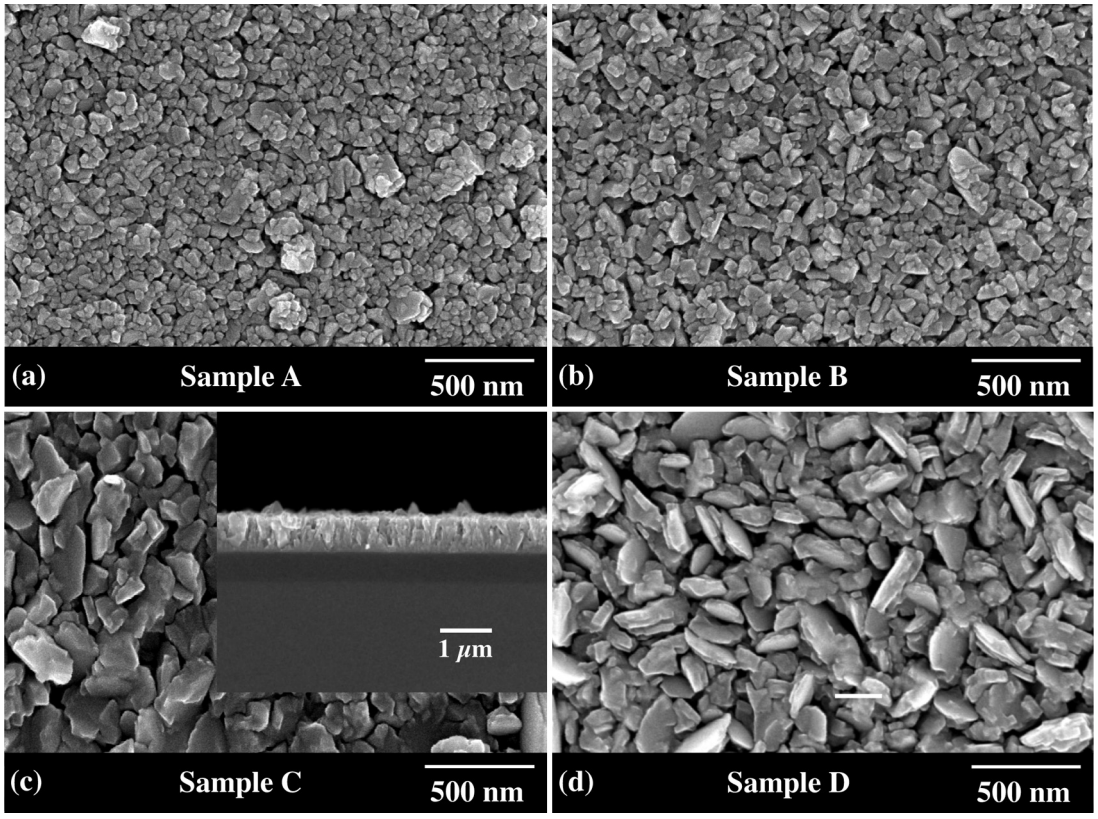

Fig. 2. FSEM images of the LNMO films deposited on stainless steel substrates, and (inset) cross-sectional FSEM image of the LNMO film deposition on the SiO_2/Si substrate.