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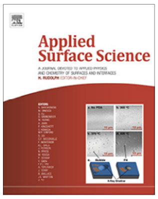

Full Length Article

Iron doped $LiCoPO_4$ thin films for lithium-ion microbatteries obtained by ns pulsed laser deposition

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ABSTRACT

Well crystallized and homogeneous iron doped $LiCoPO_4$ (LCfP) thin films have been grown by ns Pulsed Laser Ablation, at ambient temperature without any substrate heating or post-annealing treatments. The films have been deposited in vacuum and in the presence of buffer gases (O_2, Ar) and it has been found that their crystallinity, structure and morphology depend on pressure conditions. The films have been studied by Scanning Electron Microscopy and X Ray Diffraction, while their first steps of growth have been characterized by Transmission Electron Microscopy. A study of the plasma produced by the laser ablation in the different pressure conditions has been carried out with the aim of elucidate the mechanisms involved in the films deposition. LCfP thin films have been also tested as microelectrodes in lithium cells in galvanostatic condition for analyzing the reversibility of the lithium-ion battery.

1. Introduction

Lithium-ion batteries have become very important, especially in the field of portable electronics, power devices and electric vehicles, since they present characteristics of both high power density and high energy [1,2]. In the most typical formulation both positive and negative electrode materials are intercalation compounds which allow the reversible insertion of Li^+ guest ions. Several materials can be used as cathodes in Li-ion batteries, including transition metal oxides (LiMO2 with M = Co, Ni, Mn) and polyanion compounds $((XO_4)^{3-}$ with X = S, P, Si, As, Mo, W). Considering the growing necessity of power sources for miniaturized devices, the use of these materials in form of thin films for the use in microbatteries is certainly of great interest [2,3]. Among the different methods for thin films deposition, Pulsed Laser Deposition (PLD) is a method particularly suitable for the production of coating of materials with a complex stoichiometry [4,5]. PLD has been used to deposit thin films of different materials suitable for application in Li-ion cells as high potential cathodes [6]. In particular, $LiCoO_2$ [7–13], $LiMn_2O_4$ [14–20] and $LiFePO_4$ [16,21–28] thin films have been successfully deposited by several different laser wavelengths together with other more complex materials including $LiNi_{0.5}Mn_{0.5}O_2$ [29], $LiNi_{0.8}Co_{0.2}O_2$ [16,30], $LiCo_{1-x}Al_xO_2$ [13], $TiNb_2O_7$ [31], $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ [32] and Li_4SiO_4–Li_3PO_4 [33].

Thin films constituted by $LiMPO_4$ (M = Fe, Co, Mn) olivine-type transition metal orthophosphate are particularly attractive thanks to their remarkable thermal stability and battery performance. The prototypal $LiFePO_4$ (LFP) thin films have been widely studied their characteristics have been largely optimized. The isostructural $LiCoPO_4$ (LCP) olivine is also very interesting due to his high working potential [34,35]. LCP positive electrodes show in lithium cells a reversible double plateau at 4.7–4.9 V vs. Li due to the consecutive two phase lithium de-intercalation/intercalation mechanism [34]. The theoretical capacity is 167 mA h g^{-1} and the corresponding energy density is approximately 800 W h kg^{-1} to be compared to 504, 578 and 686 W h kg^{-1} for $LiCoO_2$, $LiFePO_4$, $LiMn_{1.5}Ni_{0.5}O_4$, respectively [34].

On the other hand, LCP shows small Li-ion mobility in the lattice, a quite low capacity rapidly decreasing in case of structure deterioration and poor electronic conductivity [35,36]. Metal doping of LCP, in particular iron doping, leads to a decrease the capacity fading, to an increase in the conductivity and to an improvement of the galvanostatic cycling performance [36,37].

In this work iron-doped $LiCoPO_4$ (LCfP) thin films for lithium-ion microbatteries have been fabricated using ns PLD in the presence of different gaseous environments. As mentioned above, iron doping plays a key role to enhance the electrochemical activity of this high voltage olivine in comparison to the undoped one [34,36]

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and therefore this stoichiometry has been adopted as state-of-the-art benchmark. The influence of the deposition parameters, e.g. different argon and oxygen pressures, substrate types (stainless steel and silicon) and post-annealing treatment on the crystallinity and morphology of thin films has been investigated. The structure of the deposits has been analyzed by X-ray Diffraction and Scanning Electron Microscopy, while the first steps of the films growth have been characterized by Transmission Electron Microscopy. In order to clarify the mechanism of deposition leading to the morphology and composition found in the deposited films, the plasma obtained by laser ablation in different experimental conditions, plasma often called plume for its characteristic shape, has been investigated by optical emission spectroscopy and ICCD fast imaging. As a final point, the activity of thin films of LCfP grown on S316 steel foils have been tested as positive electrode materials in lithium cells to demonstrate their reversible electrochemical activity. We would like to stress that this is the first ever reported study about the deposition of thin films constituted by high voltage olivine phases, such as the $LiCoPO_4$-based materials, and the first ever reported analysis of the assembly of these microelectrodes in lithium cells to demonstrate their electrochemical activity.

2. Experimental

The PLD experiment have been carried out by an experimental apparatus already described [38]. It consist of a stainless steel vacuum chamber equipped with windows for the inlet of the laser beam and for observation of plasma emission, with a gas inlet, a rotating target holder and a heatable substrate support. All the experiments have been performed at room temperature and the distance between the target and the substrate was kept at 1 cm. The ablation source was a Quanta System frequency doubled Nd:YAG laser with a frequency of 532 nm, a pulse duration of 10 ns and a repetition rate of 10 Hz. The laser fluence was kept at 10 J cm^{-2} and the deposition time was 2 h. The films were deposited on Si (1 0 0) and S316 steel substrates. The laser beam was incident at an angle of 45° on the target surface and the targets were $LiCo_{0.9}Fe_{0.1}PO_4$ pellets obtained by pressing a stoichiometric power synthesized by a solvothermal route [36].

The morphology of the films was analyzed by a scanning electron microscope (SEM) (Philips, FEI ESEM XL30) equipped with an Energy Dispersive X-ray Spectroscopy (EDX) apparatus, which had boron as its first detectable element. The films crystallinity was evaluated by X-ray diffraction (XRD, Siemens D5000), using Cu Kα1 radiation. The first steps of the films growth were characterized by Transmission Electron Microscopy (TEM). TEM measurements were performed by a FEI TECNAI microscope, operating at 200 kV and the material was deposited on holey carbon coated copper grids.

The optical emission spectra were detected using a fused silica 7.5 cm focal length biconvex lens focused on a bundle of 19 fused silica fibers. The bundle was linked to a 500 mm focal length spectrograph (ARC 500i) equipped with a 1200 grooves/mm grating and connected to a Princeton ICCD device (1024 × 1024 pixels). Thus, the spectral widths obtained were of about 20 nm. The gated system had best time resolution of 2 ns and each acquisition was integrated over 20 laser shots in order to increase the signal-to-noise ratio. By varying the position of the optical elements by a micrometric translation stage, it has been possible to obtain space-resolved emission spectra at different distances from the ablated target surface. The same ICCD system equipped with 105/35 mm quartz Nikkor lenses was used for acquiring gated lateral view images of the overall plasma emission (200–800 nm) induced by a single laser pulse. The spatial resolution achieved by this system was 25 μm. The acquisitions were performed by accumulating up to 5 shots, thereby avoiding previously irradiated surfaces. Both ICCD fast imaging and time-resolved spectra were accomplished by delaying the data acquisition of the plasma emission with respect to the laser pulse.

Thin films of LCfP grown onto S316 steel foils have been cut in round disks (18 mm in diameter) and directly used as positive electrodes in lithium cells. As benchmarks also composite electrode films have been prepared starting from the pristine bulk material (PLD target) and deposited on an aluminium foil by doctor-blading a slurry composed of 80% of the active material (AM), 10% of PVdF-HFP (Kynar Flex 2801) and 10% of Super P carbon in tetrahydrofuran (THF, Sigma-Aldrich). Electrodes have been tested in galvanostatic cycling in lithium cell. The galvanostatic cycling experiments have been carried out with a MTI galvanostat using ECC-STD flat cells (EL-CELL Gmbh). The cells have been prepared in an Iteco Engineering Ar-filled glovebox, by coupling the electrode under test with a lithium foil counter electrode in 1 M LiPF6 ethylene carbonate/dimethylcarbonate (EC:DMC) electrolyte solution (Solvionic), soaked on a Whatman TM glass fiber separator.

3. Results and discussion

3.1. Thin films characterization

All LCfP films were deposited starting from a target with a composition corresponding to $LiCo_{0.9}Fe_{0.1}PO_4$, in vacuum (1.5×10^{-4} Pa) and at a gas pressure of 100 Pa. Fig. 1(a) and (b) shows the XRD spectra of the films deposited on S316 steel in vacuum and at 100 Pa of oxygen. The peaks at 2Θ = 17.36, 20.72, 23.00 23.64, 25.68, 30.20, 32.52, 35.96 correspond to (2 0 0), (1 0 1), (2 1 0), (0 1 1), (1 1 1), (0 2 0), (3 0 1) and (3 1 1) reflections of crystalline LCfP [39] respectively, while the peak at 2Θ = 36.84 can be assigned to iron oxide and, since it is not present neither in the spectrum of the steel substrate nor in the spectra of the films deposited in the same conditions on Si, showing only the peaks of crystalline LCfP (Fig. 2), it is probably due to a reaction between the steel substrate and the oxygen present in the plasma produced by laser ablation of the LCfP target. Comparing the two spectra of Fig. 1(a) and (b), it is evident that the films crystallinity increases with the increase in the presence ofoxygen. Fig. 3(a) and (b) shows the SEM micrographs of the films deposited on silicon in the different pressure conditions. In all cases the films are compact and the surface seems to be formed by the coalescence of a large number of

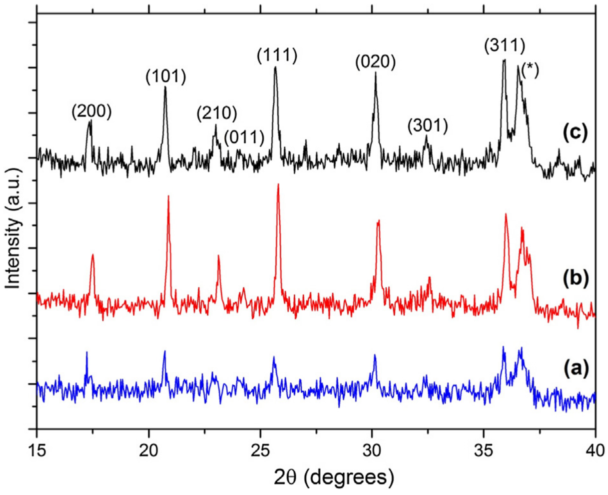

Fig. 1. XRD spectra of the films deposited on steel in vacuum (a), at 100 Pa of oxygen (b) and at 100 Pa of argon (c).