

STRUCTURE AND ELECTROCHEMICAL CHARACTERISTICS OF LiFePO_4
AS CATHODE MATERIAL FOR LITHIUM-ION BATTERIES

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To prepare cathode material for lithium batteries, LiFePO_4 powder was sputtered using an RF magnetron. Thin LiFePO_4 films were obtained on different ~ 1000 nm thick substrates. The compositional and morphological examination of these films by SEM has shown that on a silicon substrate the annealed nanocrystalline thin film of LiFePO_4 material condenses in larger monocrystals (with thin film disappearance), while such a film on the stainless steel substrate coalesces in a uniform nano-structured layer after annealing. As shown by the energy-dispersive X-ray analysis, the annealed film consists of phosphorus, iron, and oxygen in the ratio corresponding to the stoichiometric LiFePO_4 . Cyclic voltammograms of the LiFePO_4 thin layer were obtained with typical red-ox reaction peaks characterizing the electrochemical lithium insertion/extraction reactions in LiFePO_4 . The obtained thin films have a relatively high charge capacity of 127 mAh g^{-1} .

Key words: *lithium iron phosphate, thin films, lithium-ion batteries, electrochemical properties.*

1. INTRODUCTION

Recently, increased attention has been dedicated to LiFePO_4 as a promising cathode material in lithium-ion batteries for the use in consumer electronics and electrical vehicles because of the environmental compatibility and low manufacturing cost. In addition, LiFePO_4 has a relatively large theoretical capacity of 170 mAh g^{-1} , good thermal stability and low hygroscopicity [1, 2]. The main problem restricting wider application of LiFePO_4 is its low electronic conductivity and poor rate capability. Possible way to solve the above mentioned problems is to use the thin film technology and carbon addition to increase both the conductivity and the surface area of the cathode [3, 4]. To obtain well-crystallized and partly conducting LiFePO_4 thin films, in works [5–7] the radio-frequency (RF) sputter deposition was applied, while in [3] – the ionized magnetron sputter deposition technique. However, in these works little research is done on the structural and electrochemical characteristics of thin film LiFePO_4 as a cathode material in sandwich-type thin lithium batteries.

The LiFePO_4 thin films were prepared by magnetron sputtering under optimized conditions with carbon addition [8]. In the present work the sputtered thin films were tested as cathode materials for lithium ion batteries by the electrochemical impedance spectroscopy, cyclic voltammetry and cyclic potentiometry. The electrochemical characteristics of LiFePO_4 thin films were analyzed in dependence on the conditions of preparation, structure, and surface morphology.

2. EXPERIMENTAL

The LiFePO_4 (Linyi Gelon New Battery Materials Co.) sputtering target was prepared by cold pressing of the powder on a copper pad lined with indium (12 cm in diameter) for 5 min. A stainless steel lid was used to apply the pressure.

Thin films of LiFePO_4 were obtained using RF magnetron sputtering on various substrates (stainless steel, silicon, copper foil). The sputtering time was varied, with the average sputtering rate of 11 nm/min and the applied power of 300 W. The power was raised gradually in three steps (100 W \rightarrow 200 W \rightarrow 300 W) to avoid crack formation on the target surface. The subsequent annealing of the prepared LiFePO_4 film was done at 550 °C for 1 h in the argon atmosphere to increase the crystallinity of the thin films.

The surface morphology of thin layers was examined by means of a Carl Zeiss EVO 50 XVP scanning electron microscope with a facility for the energy-dispersive X-ray analysis. For electrochemical measurements, the LiFePO_4 thin film was inserted in a three-electrode cell (Fig. 1) using metallic lithium for the counter and reference electrodes. The 1 M LiClO_4 solution in propylene carbonate was used as electrolyte. A VoltaLab 40 potentiostat/galvanostat (from Radiometer Analytical) was employed for the cyclic voltammetry and charge-discharge measurements of the annealed LiFePO_4 thin films on the stainless steel and copper foil substrates. Voltage peaks at 3.5 V were not observed for thin films sputtered on the copper substrate; this implies an irreversible reaction, which indicates that there is some type of chemical reaction between the copper foil and LiFePO_4 or LiClO_4 .

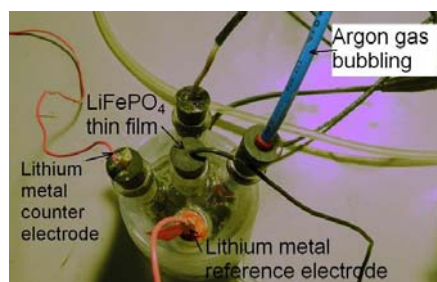


Fig. 1. The cell for electrochemical measurements of LiFePO_4 thin films.

3. RESULTS AND DISCUSSION

3.1. Structure and morphology

On the stainless steel substrate a uniform LiFePO_4 thin film is formed, which remained finely crystallized and uniform after annealing at 550 °C (Fig. 2).

After annealing, the LiFePO_4 thin film on a stainless steel substrate coalesced in a uniform nano-structured layer. The energy-dispersive X-ray spectroscopy was used to provide the composition of annealed LiFePO_4 film (the analysis was made only on the Si substrate to avoid interference from multi-compositional stainless steel alloy). It was shown that the phosphorus, iron and oxygen ratio approximately corresponds to stoichiometric LiFePO_4 (lithium metal is too light to be detected with this analysis). It is hypothesized that the tiny white grains on top of the surface are due to the growth mechanics of LiFePO_4 thin layers – small

nanocrystals form on top of the surface and continue to grow until a new layer of LiFePO_4 is developed on which the nanocrystals form again.

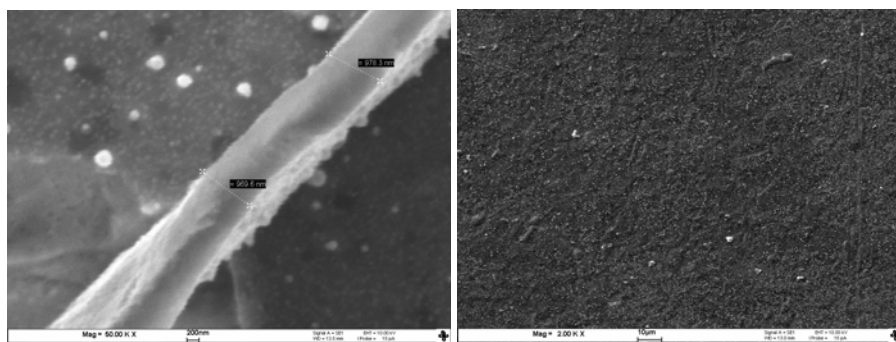


Fig. 2. SEM images of surface structure of annealed LiFePO_4 thin film on a stainless steel substrate after annealing at 550 °C (left – the film cross-section).

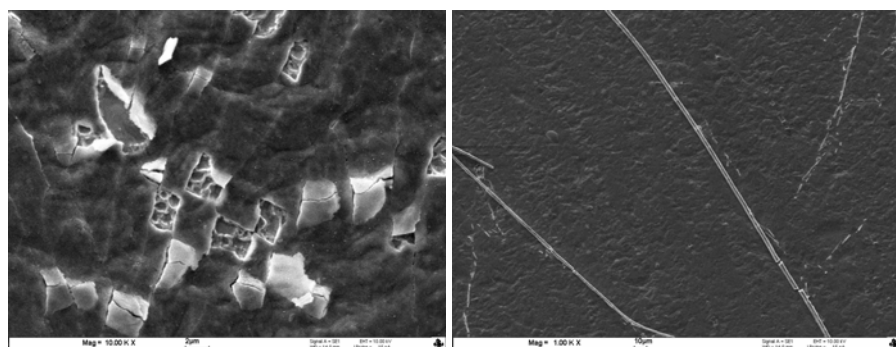


Fig. 3. SEM images of characteristic surface structures of annealed and cycled LiFePO_4 thin film on a copper foil substrate after annealing at 550°C.

The SEM pictures of the thin films sputtered on a copper foil (Fig. 3) show eroded holes on the copper foil and the channels formed on top of the layer, which evaporate after a prolonged exposure to the electron beam. This indicates the possibility of chemical interaction between the copper foil and LiClO_4 . In thin layers on the copper foil the presence of chlorine was also detected.

3.2. Electrochemical properties

The cyclic voltammogram of LiFePO_4 thin films before annealing does not show any expressed lithium ion extraction-insertion reactions (during the charging reaction the LiFePO_4 thin film cathode gives lithium ions back until a FePO_4 structure is formed, while during discharge the lithium ions are intercalating it). The annealed films exhibit an explicit couple of anodic and cathodic peaks at 3.4–3.6 V (Fig. 4). These red-ox reaction peaks characterize the electrochemical lithium insertion/extraction reactions in LiFePO_4 [1]. The ratio between the anodic and cathodic peak currents is close to 1, implying a good reversibility of lithium intercalation into and de-intercalation from a LiFePO_4 thin film. Absence of other red-ox peaks indicates that the films annealed at 550 °C consist of single-phase LiFePO_4 [9].

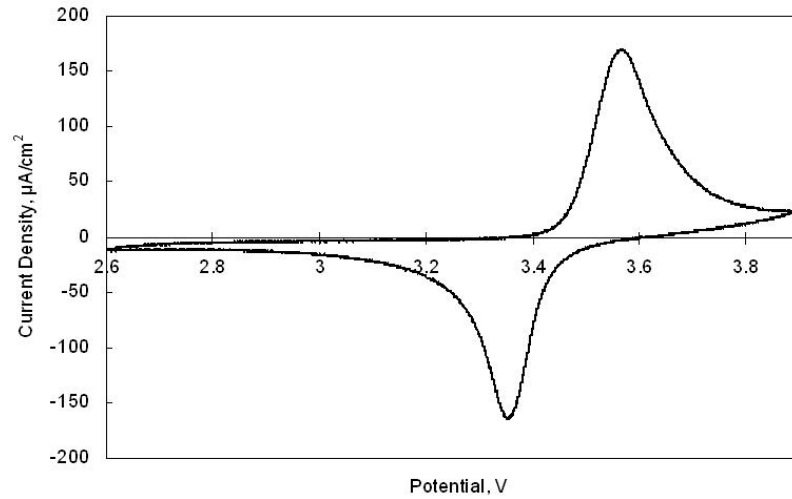


Fig. 4. Cyclic voltammogram of LiFePO₄ thin film before and after annealing (scan rate 1 mV/s).

Charge-discharge experiments on LiFePO₄ 400 nm thin films were run with the current 1 $\mu\text{A}/\text{cm}^2$ (Fig. 5), and the calculated charge capacity was 127 mAh/g. Although below the theoretical (170 mAh/g), this value is close to the capacity reported in other publications [3, 5–7].

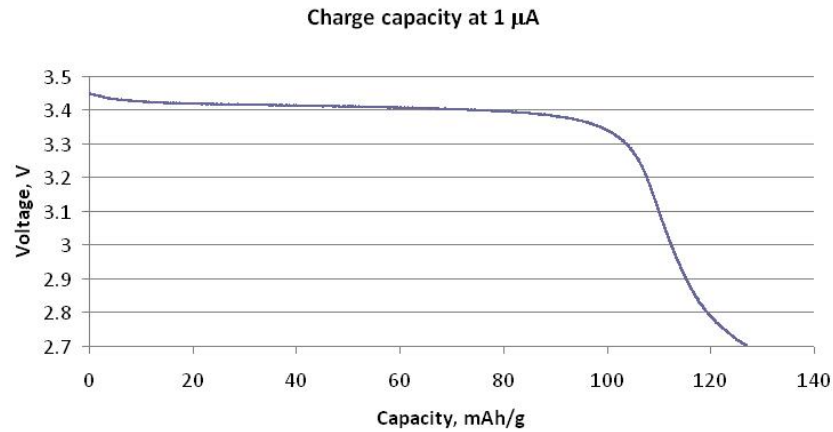


Fig. 5. Chrono-potentiometry of LiFePO₄ thin films (discharge current density 1 $\mu\text{A}/\text{cm}^2$).

4. CONCLUSIONS

Lithium iron phosphate thin films have been successfully obtained on various substrates with thickness around 1000 nm by RF magnetron sputtering method. The composition and morphology of LiFePO₄ films evidence that on the stainless steel substrate such a film coalesces in a uniform nano-structured layer after annealing. The energy-dispersive X-ray analysis confirmed that annealed films consist of phosphorus, iron and oxygen, in the ratio corresponding to the stoichiometric LiFePO₄. Typical red-ox reaction peaks obtained in cyclic voltammograms characterize the electrochemical lithium insertion/extraction reactions in

LiFePO₄ with a charge capacity of 127 mAh·g⁻¹. Absence of such red-ox reaction peaks for LiFePO₄ thin films on a copper plate is indicative of an irreversible chemical reaction during the cycling. This conclusion is supported by the SEM analysis that has shown the presence of chlorine on the film surface after cycling.

The new experimental data obtained are expected to promote further designing of multilayered lithium-ion batteries for the use in portable electrical devices and microelectronics.

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JONU BATERIJU KATODMATERIĀLA LiFePO₄ STRUKTŪRAS UN ELEKTROĶĪMISKO ĪPAŠĪBU PĒTĪJUMI

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K o p s a v i l k u m s

LiFePO₄ pulveris tika uzputināts, izmantojot RF magnetrona izputināšanas metodi. Plānās LiFePO₄ kārtiņas tika iegūtas uz dažādiem substrātiem ar biezumu līdz 1000 nm. Sastāva un morfoloģijas analīze ar SEM parādīja, ka nanokristāliskajā LiFePO₄ plānajā kārtiņā, kas uzputināta uz silīcija pamatnes, LiFePO₄ veido lielākus monokristālus, tādā veidā izjaucot plāno kārtiņu homogenitāti, savukārt uz nerūsējošā tērauda uznestā LiFePO₄ kārtiņa pēc kristalizēšanas veido viendabīgu nanostrukturētu slāni. Rentgenstaru ierosinātās fluorescences spektroskopiskā analīze kristalizētajā slānī uzrādīja fosforu, dzelzi un skābekli attiecībās, kādas pastāv stehiometriskā LiFePO₄. Cikliskās voltamperometrijas līknes pēc uzputināšanas izkarsētām kārtiņām uzrādīja red-oks maksimumus, kas raksturo elektroķīmiskās litija jonu interkalācijas un ekstrakalācijas reakcijas LiFePO₄. Iegūtās LiFePO₄ plānās kārtiņas ir ar relatīvi augstu lādiņietilpību – 127 mAh·g⁻¹.

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