Scientific Journal of Riga Technical University
Environmental and Climate Technologies

2010
Volume 4

Kinetic Behavior of $LiFePO_4$/C Thin Film Cathode Material for Lithium-Ion Batteries

Gints Kucinskis, *Institute of Solid State Physics, University of Latvia,* Gunars Bajars, *Institute of Solid State Physics, University of Latvia,* Janis Kleperis, *Institute of Solid State Physics, University of Latvia,* Janis Smits, *Institute of Solid State Physics, University of Latvia*

Abstract **– $LiFePO_4$ was prepared in a solid state synthesis with various levels of carbon content. $LiFePO_4$/C thin films were obtained via magnetron sputtering. The surface morphology and structure was examined. Electrochemical properties of $LiFePO_4$/C were studied, by using cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. Thin films acquired show a potential use as a cathode in lithium ion batteries, displaying charge capacity up to 34 mAh g^{-1}.**

Keywords **– electrochemistry, Li-ion batteries, $LiFePO_4$, thin films.**

I. INTRODUCTION

$LiFePO_4$ is a cathode material for rechargeable lithium-ion (Li-ion) batteries. $LiFePO_4$ has been recognized as promising due to its good thermal and cycling stability, environmental compatibility, low manufacturing cost and relatively high theoretical charge capacity of 170 mAh g^{-1} [1,2].

As the environmental issues caused by the burning of fossil fuels become more and more urgent, and global warming forces to lower carbon emission, it is necessary to create new, cheaper, safer and less polluting way of storing energy for green technologies such as electric vehicles (EVs). Li-ion batteries offer a relatively easy way of storing energy and have become more and more popular ever since they were first patented in 1991 by *Sony* [3]. Li-ion batteries are the most popular way of storing energy in EVs, therefore the EV Li-ion battery market is expected to grow from $ 878 million in 2009 to $ 8 billion in 2015 [4]. The low cost, high safety and high cyclability of $LiFePO_4$ make it one of the most promising cathode materials for the use in Li-ion batteries intended for EVs.

The most popular Li-ion battery cathode material is $LiCoO_2$ [3], other popular cathode materials are $LiMn_2O_4$, $LiNiO_2$ and V_2O_5 [5]. Although it is only recently that the $LiFePO_4$ batteries have emerged, 10 of 45 EV models manufactured in next 2 years will be supplied with $LiFePO_4$ batteries, making $LiFePO_4$ the most popular cathode material in Li-ion batteries intended for EVs [6].

Main problems restricting wider use of $LiFePO_4$ in Li-ion batteries are its low conductivity and poor rate capability. A possible solution for these problems is the use of the thin film technology and a carbon additive therefore increasing both the surface and the conductivity of the cathode [7,8]. So far little research has been done on the structural and electrochemical characteristics or the kinetics of $LiFePO_4$ thin films [7, 8, 9, 10, 11].

In this study $LiFePO_4$/C targets with various carbon content were prepared and sputtered using magnetron sputtering – direct current (DC), radio frequency (RF) or both combined (DC/RF). The electrochemical characteristics of $LiFePO_4$/C thin films are related to conditions of preparation, structure, surface morphology and carbon content.

II. EXPERIMENTAL

Pure $LiFePO_4$ was obtained in a solid state reaction by using stoichiometric amounts of lithium carbonate Li_2CO_3, iron oxalate $FeC_2O_4{\cdot}2H_2O$ and ammonium dihydrogen phosphate $NH_4H_2PO_4$ (all from Sigma-Aldrich, ≥99.9%) as precursor materials. For $LiFePO_4$/C sucrose or carbon black (both from Aldrich, ≥99.9%) were added.

The stoichiometric mixture of reagents was first ball milled for 30 minutes. The fine powder obtained was then inserted in a ceramic crucible and heated at a temperature of 650-750°C for 5-6 hours in a nitrogen atmosphere. A perfectly crystallized $LiFePO_4$ sample was obtained at 1100 °C at N_2 atmosphere.

$LiFePO_4$/C thin films were deposited on polished stainless steel, glass and silicon by direct current (DC), radio frequency (RF) and combined (DC/RF) magnetron sputtering. The target used for sputtering was obtained by hot pressing the $LiFePO_4$/C powder on a copper pad (150 mm in diameter) heated to 130 ºC with a pressure of 20 Pa. The sputtering time and ratio between DC and RF magnetron sputtering were varied in order to obtain various thin film thicknesses of 50 to 1000 nm. A part of the thin films was annealed at 600°C for 1 h in the argon atmosphere to increase the degree of crystallization.

The crystal structure of both thin films and $LiFePO_4$/C powder was examined by X-ray diffraction (XRD) using a Philips X'Pert Pro MPD diffractometer with CuK_α radiation and by Raman spectroscopy, using an Advantage-785 spectrometer with a laser wavelength of λ=785nm. The thin film surface morphology was characterized by scanning electron microscope (SEM) Carl Zeiss EVO 50 XVP. Electrochemical measurements were carried out in a three electrode electrochemical cell was constructed in an argon-filled glove box with a metallic Li as both counter and reference electrodes in a 1 M $LiClO_4$-PC electrolyte (PC – propylene carbonate). The electrochemical measurements of the $LiFePO_4$/C thin films were performed at 20°C and argon bubbling was performed directly in the cell before each measurement.

Cyclic voltammetry and chronopotentiometry measurements were performed by using Voltalab PGZ-301 potentiostat. Cyclic voltammetry was done for both annealed and non-annealed $LiFePO_4$/C thin films on a stainless steel substrate. Charge-discharge measurements (chronopotentiometry) were done with various current densities in a range of 1-100 µA/cm^2. Electrochemical impedance spectroscopy (EIS) was carried out at various states of charge by applying an AC signal with amplitude of 10 mV in a frequency range from 65kHz to 1 mHz using a Solartron 1287 electrochemical interface with a Solartron 1260 frequency response analyzer.

III. RESULTS AND DISCUSSION

A. Structure and Morphology

A mono-crystalline $LiFePO_4$ sample was synthesized to register the $LiFePO_4$ reference Raman spectra using 785 nm radiation (Fig. 1). Distinct peaks of Li^+ ion vibrations in the $LiFePO_4$ orthorhombic olivine structure were observed (362 and 1069 cm^{-1}) as well as sharp peaks of the bonds of PO_4^{3-} tetrahedra (573, 951, 999 cm^{-1}).

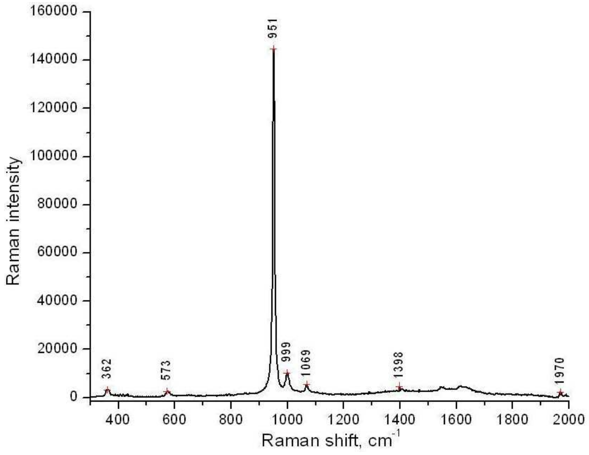

Fig. 1. Raman spectra of pure, highly crystallized $LiFePO_4$ powder.

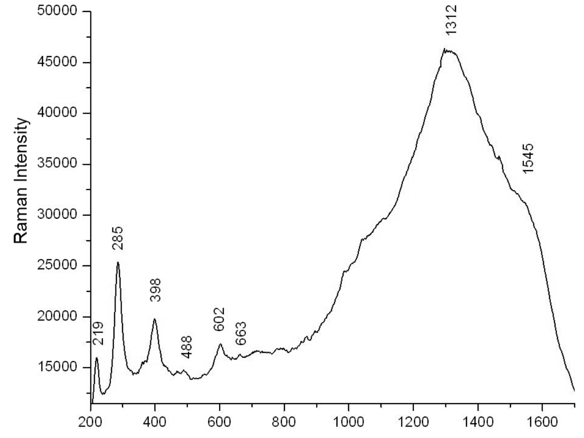

Fig. 2. Raman spectra of $LiFePO_4/C$ powder with 5 wt% carbon content.

In the Raman spectra of synthesized $LiFePO_4/C$ powder (Fig. 2) peaks corresponding to those of $LiFePO_4$ reference spectra can barely be seen in the background of the very intense and broad peeks at 1312 cm^{-1} and 1545 cm^{-1} corresponding to amorphous carbon G and D bands. It was impossible to register any Raman spectra for the $LiFePO_4$ thin films before annealing, while after annealing small Raman scattering was observed. It was too weak, however, to be interpreted.

The XRD pattern of both synthesized $LiFePO_4/C$ powder and thin films are shown in Fig. 3. All observed diffraction peaks can be indexed with the orthorhombic olivine-type structure (space group Pnmb) in agreement with the well-crystalline single phase $LiFePO_4$. Diffraction peaks of the thin film are less explicit than those of the powder sample. Nevertheless, they still indicate the same orthorhombic olivine-type structure of the single phase $LiFePO_4$.

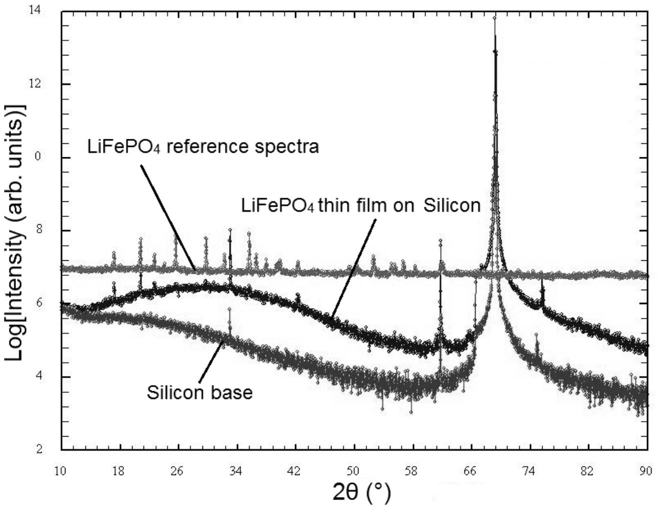

Fig 3. XRD pattern for $LiFePO_4/C$ thin films with 5 wt% carbon black content sputtered on a silicon base.

It is also noteworthy that no Fe_2P phase was observed in synthesized samples even after prolonged periods of heating in elevated temperatures as it is reported in some publications [12].

Morphological research of the $LiFePO_4$ thin film surface by SEM shows that the thin film formed on a stainless steel substrate is uniform (Fig. 4). It also stays homogenous after the annealing at 600°C. However, some $LiFePO_4$ microcrystals and bubble-like areas with lower $LiFePO_4$ densities were also observed after the annealing. It is worth noting, that on silicon substrate the nano-crystalline thin film $LiFePO_4$ material is trying to condense into larger mono-crystals thus disarranging the structure of the thin film.

The Quadrant back-scattered electron detection (QBSD) analysis of annealed $LiFePO_4/C$ thin film also showed that there is a layer of lighter elements (carbon additive) formed on top of the heavier elements of $LiFePO_4$ (Fig. 4), which proves that carbon is also deposited during the magnetron sputtering process.

It was shown by the energy-dispersive X-ray analysis, that the annealed film consists of phosphorous, oxygen and iron in relation corresponding to a stoichiometric $LiFePO_4$ (lithium is too light to be detected with this method).

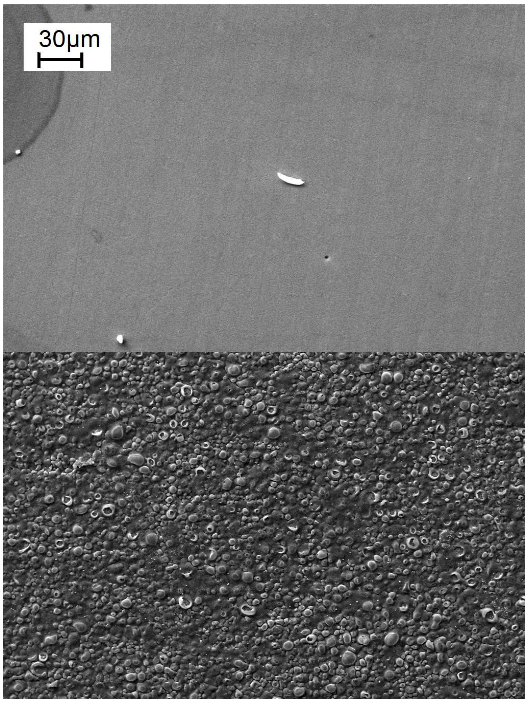

Fig. 4. SEM BQSD image of non-annealed (above) and annealed (below) 50 nm thick $LiFePO_4$ thin film on a stainless steel substrate.

B. *Electrochemical Properties*

A distinct couple of anodic and cathodic peaks are observed at 3.3 V and 3.6 V respectively for $LiFePO_4$/C thin films at the scan rate of 1 mV s^{-1} (Fig. 5) which characterize the electrochemical lithium insertion and extraction reactions from $LiFePO_4$ [1]. No other red-ox peaks were observed, which indicates that the thin films annealed at 600°C consist of single-phase $LiFePO_4$.

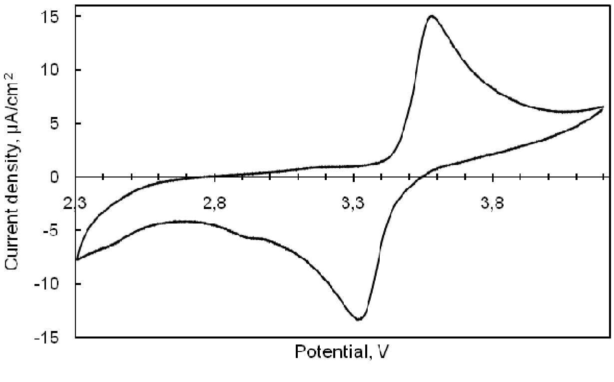

Fig. 5. Cyclic voltammogram of annealed 500 nm $LiFePO_4$/C (5 wt%) thin film (scanning rate 1 mV/s).

Weak or no red-ox peaks are observed for the non-annealed $LiFePO_4$ thin films (shown in Fig. 6), showing that lithium insertion and extraction from non-annealed $LiFePO_4$ thin films are faint or almost not present.

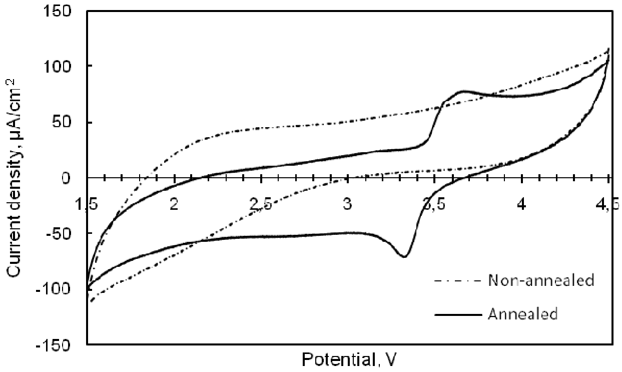

Fig. 6. Cyclic voltammogram of annealed and non-annealed 60 nm $LiFePO_4$/C (5 wt%) thin film (scanning rate 10 mV/s).

Chronopotentiometry or charge-discharge curves of $LiFePO_4$/C (5 wt%) 500 nm annealed thin film at a current density of 10 μA/cm^2 are shown in Fig. 7. The obtained discharge capacity at a cut-off voltage of 3.0 V is 34 ±5 mAh g^{-1}, which is comparable to results mentioned in other publications [9]. It was assumed that after the voltage of 3.0 V the discharge process might be shifting to other electrochemical reactions (Fig. 5).

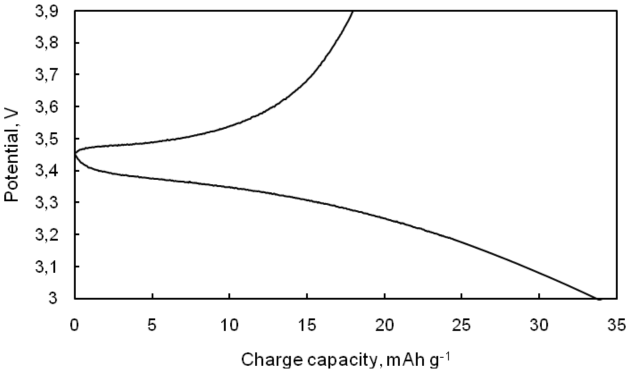

Fig 7. Charge–discharge curves of 500 nm $LiFePO_4$ thin film annealed at 600°C.

Electrochemical impedance spectroscopy (EIS) measurements which were performed for $LiFePO_4$/C thin films in three-electrode cell $LiFePO_4$/1M $LiClO_4$-PC/Li with metallic lithium as a reference and a counter electrode. The measurements in an open circuit state, charged and discharged states and during charging and discharging processes were carried out. In order to better describe the processes happening at the $LiFePO_4$/C electrode - electrolyte interface, equivalent circuits consisting of two resistances (R_e and R_{ct}), constant phase element (CPE) and Warburg element (W_0) were constructed (Fig 8). This equivalent circuit agrees with other publications [10].

During the charging and discharging processes a simplified equivalent circuit without Warburg impedance was obtained (Fig. 9) which means that under the polarization conditions the Li^+ ion diffusion is not the limiting process.

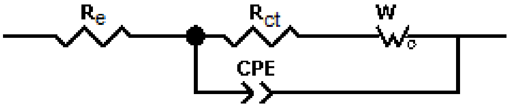

Fig 8. Equivalent circuit used for fitting experimental data for $LiFePO_4$ at various constant potentials.

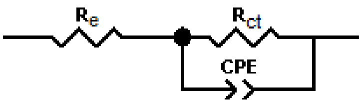

Fig 9. Equivalent circuit used for fitting experimental data for $LiFePO_4$ during charging and discharging.

Fig. 11, 12 and 13 show the Nyquist plots of the cathode at open circuit potential (OCP), discharged state and with applied charging current respectively. An intercept at the Z' axis in high frequency region represents the ohmic resistance R_e (resistance of cables, electrodes, electrolyte and $LiFePO_4$/C thin film). The semicircle in the middle frequency range indicated the charge transfer resistance (R_{ct}) of the lithium intercalation reaction. Due to the fact that the semicircle is compressed, a constant phase element CPE is introduced representing the double layer capacitance as well as in inhomogeneities on electrode/electrolyte interface. Finally, the low frequency range represents the Warburg impedance W associated with lithium-ion diffusion in $LiFePO_4$ particles.

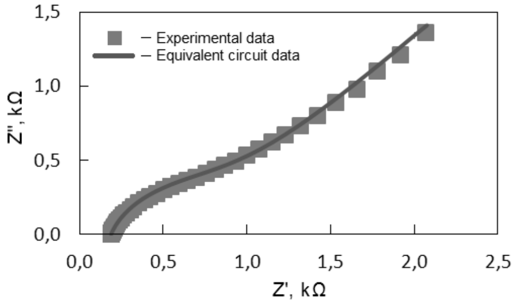

Fig. 11. Nyquist plot and equivalent circuit data for $LiFePO_4$/C 500 nm thin film at 3.4 V potential.

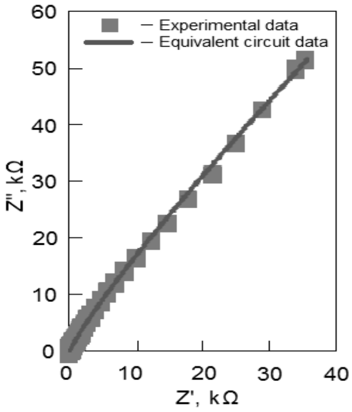

Fig. 12. Nyquist plot and equivalent circuit data for $LiFePO_4$/C 500 nm thin film at 2.7 V potential.

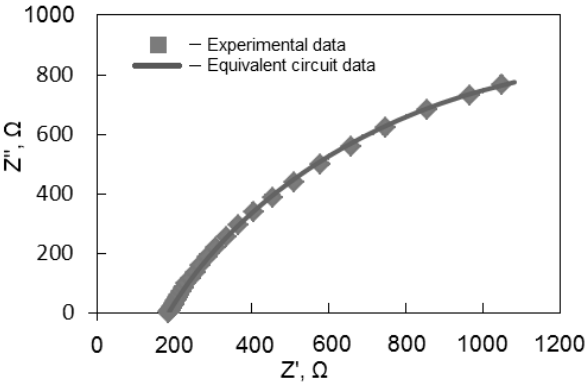

Fig. 13. Nyquist plot and equivalent circuit data for $LiFePO_4$/C 500 nm thin film with applied charging current (100 µA).

The parameters of the equivalent circuit obtained by computer simulations are presented in Table 1. The minimum value of the charge transfer resistance is acquired in a discharged state which corresponds to the maximum concentration of Li^+ ions in lithium iron phosphate. During charging, Li^+ ions are extracted from the $LiFePO_4$/C electrode which is accompanied with an increase of R_{ct}. Obviously, the highest charge transfer resistance should be when $FePO_4$ phase is dominating in $LiFePO_4$/C electrode.

TABLE 1

NUMERICAL VALUES OF THE ELEMENTS FROM EQUIVALENT CIRCUITS

	Potential E=3.4V	**Potential E=2.7V**	**Potential E=2.9V-4.1V**
R_e, Ω	188	190	187
R_{ct}, Ω	762	473	2601
W2-σ, Ω/s	1080	17012	-
CPE-Q, F	$7.2 \cdot 10^{-5}$	$5.9 \cdot 10^{-5}$	$1.11 \cdot 10^{-4}$
CPE-n	0.77	0.82	0.726

IV. CONCLUSION

The $LiFePO_4$/C powder was synthesized and sputtered on various materials using DC, RF and DC/RF magnetron sputtering methods. Compositional and morphological research of $LiFePO_4$ thin films by SEM showed that the thin $LiFePO_4$ films are carbon coated and have coalesced into a uniform nano-structured layer after annealing. Cyclic voltammograms of $LiFePO_4$ displayed explicit red-ox reaction peaks of 3.3 and 3.6 V. Obtained thin film discharge capacity was 34 mAh g^{-1}. An analysis of electrochemical impedance spectroscopy was conducted, and the three element equivalent circuit gave evidence that under the polarization conditions the Li^+ ion diffusion is not the limiting process in the $LiFePO_4$ thin film. The minimum value of charge transfer resistance is acquired in a discharged state which corresponds to the maximum concentration of Li^+ ions in lithium iron phosphate while the highest charge transfer resistance can be achieved when discharged $FePO_4$ phase is dominating in the thin film electrode.

V. ACKNOWLEDGMENTS

This work was supported by Solid State Institute of Physics, University of Latvia and Scientific Project Contest of Student Council, University of Latvia.

REFERENCES

1. Padhi A.K., Nanjundaswamy K.S., Goodenough J.B., Phospho-Olivines as Positive Electrode Materials for Rechargeable Lithium Batteries, *J.Electrochem.Soc.*, 1997, vol.144, p.1188-1194.
2. Takahashi M., Tobishima S., Takei K., Sakurai Y., Reaction behavior of $LiFePO_4$ as a cathode material for rechargeable lithium batteries, *Solid State Ionics*, 2002, vol.148, p.283-289.
3. Kiehne H.A., *Battery Technology Handbook, Second edition*, New York: Marcel Dekker Inc., 2003. ISBN: 0-8247-4249-4.
4. Pike Research. Lithium Ion Batteries for Electric Vehicles to Approach $8 Billion in Sales by 2015. *PikeResearch.com* [Online] 2009, [reference 28.06.2010.] http://www.pikeresearch.com/newsroom/lithium-ion-batteries-for-electric-vehicles-to-approach-8-billion-in-sales-by-2015.
5. Patil A., Patil V., Shin D.W., Choi J.-W., Paik D.-S., Yoon S.-J., Issues and Challenges Facing Rechargeable Thin Film Lithium Batteries, *Materials Research Bulletin*, 2008, vol.43, p.1913-1942.
6. Green Car Congress. Forecast: Lithium Ion Batteries for Electric Vehicles to Approach $8 Billion in Sales by 2015, www.greencarcongress.com [online] 2009, [reference 28.06.2010.] http://www.greencarcongress.com/2009/12/pike-liion-20091203.html.
7. Chiu K.-F., Chen P.Y., Structural evolution and electrochemical performance of $LiFePO_4$/C thin films deposited by ionized magnetron sputtering, *Surface & Coatings Technology*, 2008, vol.203, p.872-875.
8. Eftekhari A., Surface Modification of Thin-Film Based $LiCoPO_4$ 5V Cathode with Metal Oxide, *J. Electrochem. Soc.*, 2004, vol.151, 1816-1819.
9. Xie J., Imanishi N., Zhang T., Hirano A., Takeda Y., Yamamoto O., Li-ion diffusion kinetics in $LiFePO_4$ thin film prepared by radio frequency magnetron sputtering, *Electrochimica Acta*, 2009, vol.54, p.4631-4637.
10. Gao F., Tang Z., Kinetic behavior of $LiFePO_4$/C cathode material for lithium-ion batteries, *Electrochimica Acta*, 2008, vol.53, 5071-5075.
11. Yada C., Iriyama Y., Jeong S.-K., Abe T., Inaba M., Ogumi Z., Electrochemical properties of $LiFePO_4$ thin films prepared by pulsed laser deposition *J.Power Sources*, 2005, vol.146, p.559-564.
12. Kanga H.-C., Juna D.-K., Jinb B., Jina E.M., Parka K.-H., Gua H.B., Kimc K.-W., Optimised solid-state synthesis of LiFePO4 cathode materials using ball milling, *Journal of Power Sources*, 2008, vol.179, p.340-346.

Gints Kucinskis, BSc.phys, Engineer
Solid State Institute of Physics, University of Latvia
Address: 8 Kengaraga Street, LV-1063, Riga, Latvia
Phone: +37126479194, Fax: +37167132778
e-mail: gints.kucinskis@gmail.com

Gunars Bajars, Dr.chem, Leading Researcher
Solid State Institute of Physics, University of Latvia
Address: 8 Kengaraga Street, LV-1063, Riga, Latvia
Phone: +37129579841, Fax: +37167132778
e-mail: bajars@lu.lv

Janis Kleperis, Dr .phys, Head of Laboratory
Solid State Institute of Physics, University of Latvia
Address: 8 Kengaraga Street, LV-1063, Riga, Latvia
Phone: +371 7260538, Fax: +37167132778
e-mail: kleperis@lu.lv

Janis Smits,
Solid State Institute of Physics, University of Latvia
Address: 8 Kengaraga Street, LV-1063, Riga, Latvia
Phone: +37126479194, Fax: +37167132778
e-mail: smits@lu.lv

Gints Kučinskis, Gunārs Bajārs, Jānis Kleperis, Jānis Šmits. $LiFePO_4$/C plāno kārtiņu litija jonu bateriju katodmateriāla kinētiskās īpašības

Litija dzelzs fosfāts ($LiFePO_4$) ir daudzsološs litija jonu bateriju katodmateriāls tā lielā uzlādes – izlādes reižu skaita, augstās drošības, zemo izmaksu un labās teorētiskās lādiņietilpības dēļ. Pēdējā laikā tas kļūst īpaši populārs kā katodmateriāls elektriskajiem automobiļiem paredzētajos litija jonu akumulatoros. Tā galvenais trūkums ir zemā elektrovadītspēja, kas neļauj attīstīt augstu jaudu maza un vidēja izmēra baterijām.

Darbā $LiFePO_4$ ir sintezēts no Li_2CO_3, $FeC_2O_4{\cdot}2H_2O$ un $NH_4H_2PO_4$ cietvielu sintēzes ceļā. Ir veikta $LiFePO_4$ struktūras analīze. Ar līdzstrāvas, radiofrekvenču un kombinēto magnetrona izputināšanas metodi iegūtas $LiFePO_4$ plānās kārtiņas (60 nm – 1500 nm biezas), daļa no tām tiek kristalizētas. Kārtiņām ir veikta sastāva, struktūras un morfoloģijas analīze. Darbā ir izdarīti elektroķīmiskie mērījumi $LiFePO_4$/1 M $LiClO_4$-PC/Li elektroķīmiskajā šūnā ar Li references elektrodu: cikliskā voltamperometrija, izlāde-uzlāde (hronopotenciometrija), elektroķīmiskā impedances spektroskopija (EIS). Ir konstruētas EIS rezultātus aprakstošas ekvivalentās shēmas.

Veiktā cikliskā voltamperometrija $LiFePO_4$ plānajām kārtiņām uzrādīja stabilu Li^+ jonu interkalācijas spriegumu 3,45 V ar uzlādes un izlādes reakciju maksimumiem atbilstoši pie 3,6 V un 3,3 V. Iegūto plāno kārtiņu gravimetriskā ietilpība (līdz 34 mAh g^{-1}) ir salīdzināma ar literatūrā minēto. Elektroķīmiskās impedances spektroskopijas rezultāti liecina, ka lādiņa pārneses pretestība ir lielāka, ja Li^+ jonu daudzums $LiFePO_4$ ir mazāks, tātad lādiņa pārneses pretestība palielinās līdz ar $FePO_4$ fāzes īpatsvara palielināšanos $LiFePO_4$.

Гинтс Кучинскис, Гунарс Баярс, Янис Клеперис, Янис Шмитс. Кинетические характеристики $LiFePO_4$/C тонких пленок как катодного материала в литий-ионных батареях

Литий-железофосфат ($LiFePO_4$) является перспективным катодным материалом для литий-ионных батарей ввиду достаточно большого срока эксплуатации, высокого уровня безопасности, низкой стоимости и хорошей теоретической емкости заряда. В последние время $LiFePO_4$ становится особенно популярным катодным материалом в литий-ионных аккумуляторах, предусмотренных для электромобилей. Его основным недостатком является низкая электропроводность, которая препятствует развитию высокой мощности батареи малых и средних размеров.

В данной работе $LiFePO_4$ синтезирован из Li_2CO_3, FeC_2O_4 • $2H_2O$ и $NH_4H_2PO_4$ методом твердофазного синтеза. Проведен анализ структуры $LiFePO_4$. Тонкие пленки (60 нм - 1500 нм) $LiFePO_4$ получены разными методами магнитного распыления, некоторые из них дополнительно кристаллизованы. Для тонких пленок $LiFePO_4$ проведен анализ состава, структуры и морфологии. Электрохимические измерения проводились в электрохимической ячейке $LiFePO_4$/1 M $LiClO_4$-PC/Li с Li электродом сравнения: циклическая вольтамперометрия, кривые разряда-заряда, электрохимическая импедансная спектроскопия (ЭИС). Моделированы эквивалентные схемы, описивающие результаты ЭИС.

Исследования $LiFePO_4$ циклической вольтамперометрии показали стабильный потенциал интеркаляции ионов лития в области 3,45 В с максимумами тока при 3,6 В и 3,3 В для зарядки / разрядки соответственно. Гравиметрическая емкость тонких пленок (до 34 мАч $г^{-1}$) сравнима с литературными данными. Результаты электрохимической импедансной спектроскопии показали, что сопротивление переноса заряда больше, если количество Li^+ ионов в $LiFePO_4$ меньше, следовательно, сопротивление переноса заряда возрастает с увеличением доли фазы $FePO_4$ в $LiFePO_4$.