Using the Atomic-Layer-Deposited method to obtain LiFePO4 film: The influence of process conditions on the phase composition of the film

A.V. Dolganov, O.Y. Chernyaeva, E.N. Lyutova, V.M. Kyashkin, K.N. Nishchev
Mordovian Ogarev State University, Saransk 430005, Russia
E-mail: dolganov_sasha@mail.ru (A.V. Dolganov).

The approach to synthesis of LiFePO4 using the atomic layer deposited method (ALD-method) is offered and basic laws of the process revealed. Influence of synthesis conditions, precursors' nature and the sequence of their introduction into the reactor upon the phase composition and morphology of the formed films was studied. The phase composition of the film obtained with the use of ALD-method was investigated in details using a wide series of physical and chemical methods.

Keywords: Atomic layer deposited method (ALD-method), LiFePO$_4$ film.

1. Introduction

One can hardly imagine modern life without various gadgets and electro transport. They require special power supply – high-energetic, easy, durable, safe, cheap and reliable [1]. Currently, these requirements are most successfully fulfilled by Li-ion batteries (LIBs), moreover their electrochemical characteristics are continuously improved because of the intensive research of their properties [2, 3]. Specific characteristics of LIBs are much better than those of lead-acid, nickel-cadmium, nickel-metal hydride batteries having been recently used. They possess high specific electrochemical characteristics and are safe for environment in comparison with traditional chemical electrical supplies [4]. High values of density of LIBs energy cause their wide application as self-contained electric sources to power all kinds of electronic equipment. They are irreplaceable in transport, in cars, in industry, in space vehicles, in military technology and in many other areas of modern life. High specific energy, high security, favorable ratio of price/performance, no memory effect makes LIBs very popular [5]. Electrochemical characteristics of LIBs strongly depend on structure and properties of active electrode stuffs and electrolytes, especially on characteristics of cathodic stuffs. At present complex oxides of transitive metals and lithium, such as $LiCoO_2$, $LiMn_2O_4$, and also bonds on the basis of polyanions for example $LiFePO_4$ are used as cathodic materials in batteries [6,7]. Lithiated iron phosphate LiFePO$_4$ with the structure of olivine, offered as a cathodic stuff for batteries recharged lithium-ionic, is rather perspective for accumulators of new genera-

tion since theoretical container of this stuff is high (170 mA h/g) [8-9]. Besides, this stuff is ecologically safe, thermally steady in completely charged state. The low cost price of LiFePO$_4$ is also important. The analysis of publications has shown that in order to achieve high efficiency of such cathodic stuff it is necessary to supervise or operate particle size, morphology and interaction between particles of crystal LiFePO$_4$[10-12]. In spite of the fact that lithium of iron phosphate researches have been proceeded for a long time, the number of publications devoted to the problem of searching new approaches to synthesis of nanosized particles LiFePO$_4$, is rapidly growing [13-15]. It is mainly connected with the tendencies of microminiaturisation of electronic devices, and as consequence of it, with working out of essentially different attitudes to getting thin-film nanosized materials of new generation possessing set capacitor characteristics, dimensions and morphology. For these purposes there have been widely used such methods as chemical and plasma chemical gas phase deposition, vacuum deposition processes, including thermal vacuum spraying, magnetron sputtering, vacuum arc deposition, ion beam deposition, electron beam deposition [16,17]. However, all these methods are not suitable for nanoscale films based on LiFePO$_4$. Currently, to create thin film materials a new approach by using atomic layer deposited method (ALD- method) is actively developing. Herein, we studied the possibility of applying the ALD-method for nanoscale films based on LiFePO$_4$, using the following precursors: ($FeCl_2$), (($CH_3O)_3PO$), tert-butylate lithium (LiOtBu) and distilled water (H_2O).

2. Material and methods

2.1. Materials

Crystalline silicon Si (100) was chosen as a substrate. The silicon was cleaned three times with acetone, then washed with ethanol in order to remove various fats and dirt. Then it was dried with compressed air.

Ferrocene (Fc), $FeCl_2$ (98%, Sigma Aldrich), trimethylphosphate ($(CH_3O)_3PO$), TMPO) (97%, Sigma Aldrich), lithium t -butoxide (t-BuOLi) (97%, Sigma Aldrich) and water (H_2O) were used as precursors. Nitrogen acted as an inert gas to purge the reactor of excess precursor and reaction products.

The layers were deposited by atomic layer deposition in a Beneq TFS 200 ALD reactor. The process temperature deposition was 300 ºC. One ALD cycle for obtaining a film forms the following combination: LiO^{t}Bu (1 sec pulse/10 s purge) + H_2O (1 sec pulse/10sec purge) + $FeCl_2$ (1 sec pulse/10 sec purge) + H_2O (1 sec pulse/10 sec purge) + TMPO (2 sec pulse /10 sec purge) + H_2O (1 sec pulse/10 sec purge). Thus, the amorphous film can be obtained by repeating the above ALD cycle. After synthesis the amorphous film was being annealed at 500 ºC for one hour in argon atmosphere to obtain a crystalline structure.

Diffractograms (XRD) of the samples were recorded on an EMPYREAN PANalytical X-ray diffractometer with copper radiation (λ = 1.5418 Å) at room temperature. To analyze the diffractograms, we used the PDF-2 database of the international diffraction data center. Film surface morphology was studied by means of scanning probing microscope (SPM) SPM 9600 of the firm SHIMADZU. Elementary analysis of the samples of the obtained films was carried out using the X-ray fluorescence (automatic wave serial) ARL PERFORM'X 4200 spectrometer from THERMO Fisher SCIENTIFIC (Switzerland).

3. Results and discussion

The possibility of synthesis LiFePO$_4$ using atomic layer deposited technology (ALD-technology) is caused by uniqueness atomic-layer deposition method, namely, the ability to form layers with a given ratio of elements in the film. Since the process of synthesis with ALD-technology use is multiphase and multistage, the choice of optimum conditions of synthesis has become non trivial problem. We have to consider important set of parameters, which should be treated simultaneously: temperature, the nature of precursor, pulse and purge time, and also the nature of a substrate and its superficial activity in the conditions of atomic layer deposited synthesis.

On the basis of the special requirements applied to precursors, the following precursors have been selected to carry out atomic layer deposited process: ferrocene (Fc) and $FeCl_2$ have been chosen as source of Fe(II), triethyl phosphate ($(CH_3O)_3PO$) for obtaining element PO_4^{3-} and tert-butylate lithium (LiO^{t}Bu) were used as a source of element Li(I). Water (H_2O) was used to transfer salt of metals into oxides.

The use of ferrocene is really convenient (the presence of target Fe(II), due to easy thermal decomposition of it and assumed simplicity of stoichiometry occurring during chemical reactions. However, with all the positive moments, the use of ferrocene as a precursor in atomic-layer-deposited method is not possible, because at heating it sublimes and decomposes to form a mixture of products consisting not only of compounds of iron(II) but iron (III) compounds of iron mixed-valence and metallic iron [18-22]. Use of precursor $FeCl_2$ has allowed receiving iron in the necessary oxidation state, namely FeO.

Optimum selection of interrelation Li:Fe:P while obtaining LiFePO$_4$ seems to be very important as both surplus and a lack of one of three elements can lead to getting secondary phases, and in certain cases to their full domination [23]. The optimal ratio of Li:Fe:P is 1:1:1 judging by the basis of literary data and the analysis of the phospho-olivines crystal structure [23].

The growth of the film in ALD-process is due to the chemisorption of the precursor with the substrate surface, i.e. the chemical interaction with the substrate or active groups on its surface proceeds. Therefore, in the case of the development of three-component systems, the reactivity of the precursors used is of particular importance with respect to both the functional groups contained on the surface of the substrate and among themselves [24]. We have studied and optimized the reactions of each precursor with water. To this purpose we made a series of experiments - for each precursor ($FeCl_2$, $(CH_3O)_3PO$, LiO^{t}Bu) the reactions with water have been made with the ALD-method at 300 °C, setting time of pulse 200, 400, 600, 800, 1000 ms, and purge time 2, 4, 6, 8, 10 sec, accordingly. Both flow meters have been set on standard values for this installation - 250 cm^3/minutes. Investigation of samples by means of scanning probing microscope (SPM) has shown that the increase of pulse and purge time has negative influence on the growth and uniformity of film growth. It was found that the most equable film growth was scored at 200 ms, and purge time 2 sec (Fig. 1-3). The analysis of SPM data showed that t-butylate lithium has the highest speed of interaction with the silicon surface (Fig.1). The iron chloride(II) has a lower rate of reactivity with hydroxyl groups on the surface of the substrate than
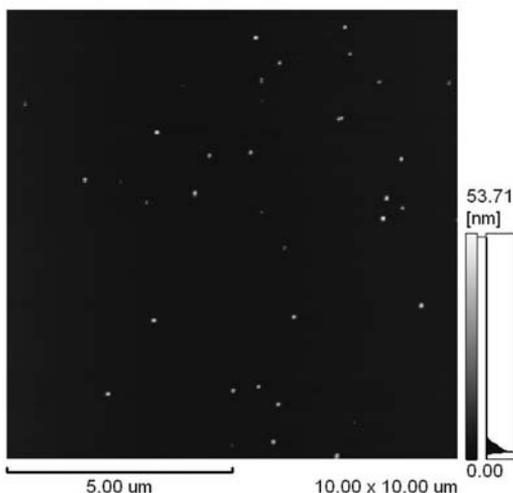
Fig. 1. SPM images film Li2O, obtained out of precursors LiO^{t}Bu and H$_2$O by ALD-method. Condition: precursors pulse time 200 ms and time of purge 2 sec.
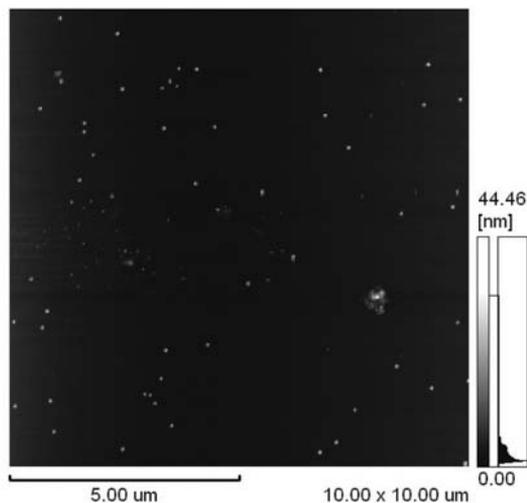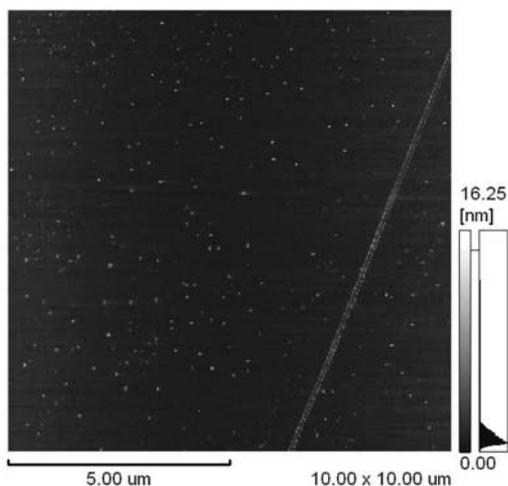

Fig. 2. SPM images film FeO, obtained out of precursors FeCl$_2$ and H$_2$O ALD-method. Condition: precursors pulse time 200 ms and time of purge 2 sec.

Fig. 3. SPM images film PO$_x$, obtained out of precursors CH$_3$O)$_3$PO and H$_2$O by ALD-method. Condition: precursors pulse time 200 ms and time of purge 2 sec.

t-butylate lithium (Fig.2), and the interaction of tri-methyl phosphate with the hydroxyl groups on the surface of the substrate is going on extremely slow (Fig.3).

Thus, on the basis of the received data the following scheme of LiFePO$_4$ synthesis with ALD-method use was suggested (Fig. 4).

After the experiment in order to evaluate the ratio of the elements (mass fraction) in the film we conducted x-ray fluorescence analysis of the obtained films the results of which are shown in Table 1.

Analysis of data obtained has shown that per cent ratio of the elements Fe:P does not correspond to the calculated theoretical value (theoretical ratio of Fe: P in LiFePO$_4$ is equal to 1,75). Practical ratio is 5.35. Such a high ratio indicates the possibility of formation of LiFePO$_4$ in addition to other iron-containing compounds. This assumption was confirmed by the study of the film obtained using the method of XRF analysis (see below). In our opin-
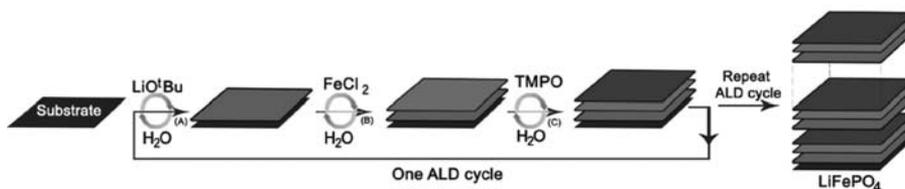

Fig. 4. Scheme of application of atomic layer of amorphous LiFePO$_4$ at 300 °C with the use of precursors of iron chloride(II) (FeCl$_2$), trimethyl phosphate, ((CH$_3$O)$_3$PO), water (H$_2$O) and tert-butylate lithium (LiO^{t}Bu). Conditions: a) sequential pulse of LiO^{t}Bu and H$_2$O leading to formation of Li$_2$O layer (red) b) sequential pulse FeCl$_2$ and H$_2$O, leading to the growth of the FeO layer (green); c) serial pulse (CH$_3$O)$_3$PO and H$_2$O that leads to the deposition of layer POx (blue). One ALD cycle for the growth of amorphous LiFePO$_4$ consists of stages (a) - (c). Settings pulse/purge of each precursor - 200 ms. pulse/2 sec. purge.

X-ray fluorescence analysis

Element	Mass fraction, %
Fe	69, 60
P_x	12, 83
Si	0, 442

T**he results of x-ray fluorescence analysis after optimizing the supply of the precursor to TMPO**

Time pulse TMPO, sec	Ratio Fe:P
1,0	5,35
1,2	5,19
1,4	4,67
1,6	4,34
1,8	3,65
2,0	3,21
2,2	3,23
2,4	3,25

Fig. 5. Experimental (a) and calculated for $LiFe_5O_8$, Li_3PO_4, $Fe_{1,987}O_3$, $LiFePO_4$ XRD pattern
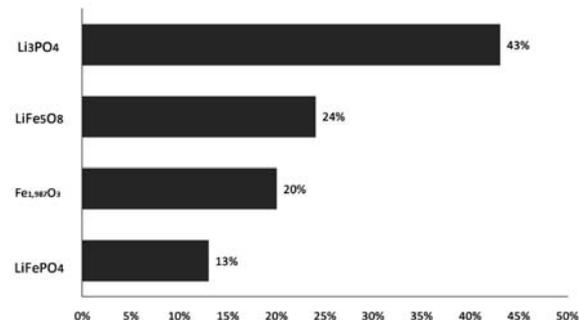
Fig. 6. Diagramme of a percentage ratio of phases in crystalline structure of the film.

ion, it descends owing to low FeO monomolecular layer. Concentration of phosphorus in the film can be raised in several ways, in particular by time prolongation in TMPO precursor delivering into reaction camera. The results of some experiments are given in table 2.

The table 2 shows that the variation of the conditions of the precursor purge time reduced the ratio of Fe:P in the film to the value of 3.2. Further optimization of the parameters leads to a decrease in the ratio Fe:P which confirms the assumption of a low reactivity of the TMPO.

The film obtained in the conditions of the process of atomic layer deposition is X-ray amorphous, that is, to further identification of the obtained phases, it is necessary to transform the amorphous state onto crystalline structure. For this, the substrates were annealed at 500 °C since according to literature data at the temperatures above 500 °C the structural type olivine is transformed into other particular phases. After annealing the sample was investigated with the method of XRD. The resulting diffraction pattern is shown in Fig. 5(a).

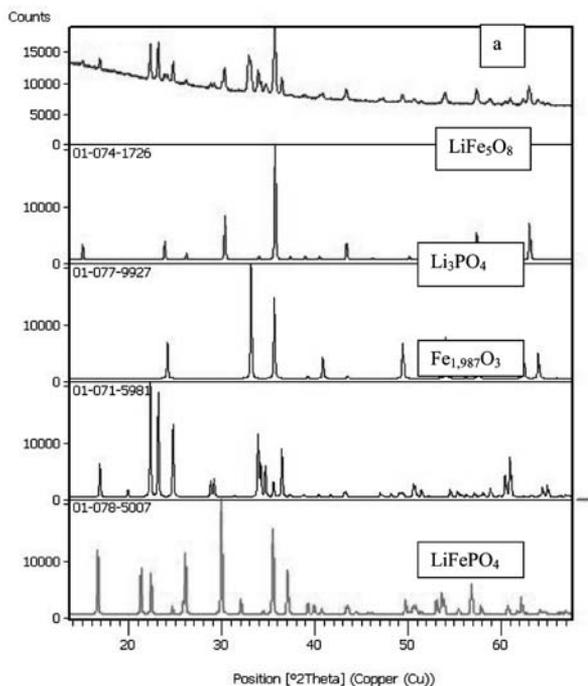Analysis of the obtained diffraction pattern in comparison with the reference diffractogramme

shows the formation of four phases: $LiFe_5O_8$, Li_3PO_4, $Fe_{1,987}O_3$, $LiFePO_4$. According to semiquantitative analysis with the calculation method of corundum numbers the percentage of the target phase $LiFePO_4$ was 13 % (Fig.6).

In our opinion, the formation of phase Li_3PO_4 in the conditions of annealing is possible with its low value of standard enthalpy of formation $\Delta H_f^0 =$ 2982,09 kJ • mol^{-1} [25] which makes the stated phase to be the most energetically favourable amorphous film at annealing. Phase $LiFe_5O_8$ has structural type spinel and is formed at interaction (fusion) Fe_2O_3 with Li_2O, the named process is described in work [26].

Fe_2O_3 is formed owing to the process of FeO dispro-portionation before the formation of Fe_2O_3 and Fe in the following reaction:

4FeO $^{200 - 565\,°C}$ Fe_3O_4 + Fe.
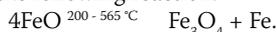
A detailed mechanism for the formation of sec-ondary phases as well as ways to suppress their growth at the present time is investigated in detail.

4. Conclusions

Thus, the process of obtaining LiFePO$_4$ film us-ing the atomic-layer-deposited method has been studied thoroughly. The influence of the precur-sors nature upon the composition and morphol-ogy of the film formed is determined. It is shown that the choice of the precursor introduction se-quence strongly influences the formation of a film of a final given composition. The reactivity of pre-cursors with respect to the substrate was studied it was found that lithium *tert*-butylate had the maxi-mum reactivity, then iron (II) chloride, and trimeth-yl phosphate demonstrated the lowest reactivity.

References

[1] N. Lewis, D. Nocera, Powering the plan-et: Chemical challenges in solar energy utiliza-tion, Proc. Nat. Acad .Sci. USA. 103 (2006) 15729-15735.

[2] F. Croce, A. Epifanio, J. Hassoun, A. Deptu-la, T. Olczac, B. Scrosati, A Novel Concept for the Synthesis of an Improved LiFePO$_4$ Lithium Battery Cathode, Electrochemical and Solid-State Letters. 5 (2002) 47-50.

[3] C.M. Julien, A. Mauger, K. Zaghib, H. Groult, Comparative Issues of Cathode Ma-terials for Li-Ion Batteries, Inorganics. 2 (2014) 132-154.

[4] J.R. Dahn, E.W. Fuller, M. Obrovac, U. Yon, Sacken Thermal stability of Li$_x$CoO$_2$, Li$_x$NiO$_2$ and λ-MnO$_2$ and consequences for the safety of Li-ion cells, Solid State Ionics. 69 (1994) 265-270.

[5] M. Stanley, Whittongham, Lithium Bat-teries and Cathode Materials, Materials Chem. Rev. 104 (2004) 4271-4302.

[6] L. Dimesso, C. Förster, W. Jaegermann, J.P. Khanderi, H. Tempel, A. Popp, J. Engstler , J.J. Schneider, A. Sarapulova, D. Mikhailova, L.A. Schmitt, S. Oswald, H. Enrenberg, Devel-opments in nanostructured LiMPO$_4$ (M = Fe, Co, Ni, Mn) composites based on three dimensional

carbon architecture, Chem. Soc. Rev. 41 (2012) 5068-5080.

[7] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goo-denough, Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries, J. Electrochem. Soc. 144 (1997) 1188-1194.

[8] J.Z. Zhang, L. Zhang, J.A. Schlueter, P.S. Redfern, L. Curtiss, K. Amine, Understanding the redox shuttle stability of 3,5-di- tert-butyl-1,2-di-methoxybenzene for overcharge protection of lith-ium-ion batteries, J. Power Sources. 195 (2010) 4957-4962.

[9] A.V. Churikova, A.V. Ivanishchev, I.A. Ivan-ishcheva, V.O. Sycheva, N.R. Khasanova, E.V. Anti-pov, Determination of lithium diffusion coefficient in LiFePO$_4$ electrode by galvanostatic and poten-tiostatic intermittent titration techniques, Electro-chim. Acta. 55 (2010) 2939-2950.

[10] L. Wang , X. He, W. Sun , J. Wang, Y. Li, S. Fan, Crystal Orientation Tuning of LiFePO$_4$ Nano-plates for High Rate Lithium Battery Cathode Ma-terials, Nano Lett. 12 (2012) 5632-5636.

[11] K. Saravanan, M.V. Reddy, P. Balaya, H. Gong , B.V.R. Chowdari, J.J. Vittal, Storage perfor-mance of LiFePO$_4$ nanoplates, J. Mater. Chem. 19 (2009) 605-610.

[12] N. Meethong , Y.H. Kao , S.A. Speakman , Y.M. Chiang, Aliovalent Substitutions in Oliv-ine Lithium Iron Phosphate and Impact on Struc-ture and Properties, Adv. Funct. Mater. 19 (2009) 1060-1070.

[13] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, Phospho-olivines as Positive-Elec-trode Materials for Rechargeable Lithium Batteries, J. Electrochem. Soc. 144 (1997) 1188-1194.

[14] R. Dominko , M. Bele , M. Gaberscek , M. Remskar , D. Hanzel , J.M. Goupil , S. Pejovnik, J. Jamnik, Porous olivine composites synthesized by sol–gel technique, J. Power Sources. 153 (2006) 274-280.

[15] S. Yang, P.Y. Zavalij, M.S. Whittingham, Hydrothermal synthesis of lithium iron phosphate cathodes, Electrochem. Commun. 3 (2001) 505-508.

[16] M.R. Yang, T.H. Teng, S.H. Wu, Hydrother-mal synthesis of lithium iron phosphate cathodes, J. Power Sources. 159 (2006) 307-311.

[17] G. Arnold, J. Garche, R. Hemmer, S. Strö-bele, C. Vogler, M. Wohlfahrt-Mehrens, LiFePO$_4$/carbon cathode materials prepared by ultrasonic spray pyrolysis, J. Power Sources. 119 (2003) 247-251.

[18] N. Koprinarov, M. Konstantinova, M. Ma-rinov, Ferromagnetic Nanomaterials Obtained by Thermal Decomposition of Ferrocene, Solid State Phenomena. 159 (2010) 105-108.

[19] E.P. Sajitha, V. Prasad, S.V. Subramanyam, A.K. Mishra, S. Sarkar, C. Bansal, Structural, magnetic and Mössbauer studies of iron inclusions in a carbon matrix, J. Magn. Magn. Mater. 313 (2007) 329-336.

[20] M. Rooth, A. Johansson, M. Boman, A. Hårsta, Atomic Layer Deposition of Iron Oxide Thin Films and Nanotubes using Ferrocene and Oxygen as Precursors, Chem. Vap. Deposition. 14 (2008) 67–70.

[21] A. Barreiro, S. Hampel, M.H. Rümmeli, C.K. Kramberger, A. Grüneis, K. Biedermann, A. Leonhardt, T. Gemming, B. Büchner, A. Bachtold, T. Pichler, Thermal Decomposition of Ferrocene as a Method for Production of Single-Walled Carbon Nanotubes without Additional Carbon Sources, J. Phys. Chem. B. 110(2006) 20973-20977.

[22] A. Leonhardt, S. Hampel, C. Muller, I. Mönch, R. Koseva, M. Ritschel, D. Elefant, K. Biedermann, B. Büchner, Synthesis, Properties, and Applications of Ferromagnetic-Filled Carbon Nanotubes, Chem. Vap. Deposition. 12 (2006) 380–387.

[23] S. Ping Ong, L. Wang, B. Kang, G. Ceder, Li–Fe–P–O_2 Phase Diagram from First Principles Calculations, Chem. Mater. 20 (2008) 1798-1807.

[24] T. Kääriäinen, D. Cameron, M.-L. Kääriäinen, A. Sherman, Atomic Layer Deposition Principles, Characteristics, and Nanotechnology Applications, 2nd ed. John Wiley New York 2013.

[25] A. Iglesia, Estimating the thermodynamic properties of phosphate minerals at high and low temperature from the sum of constituent units, Estudios Geol. 65 (2009) 109-119.

[26] L.A. de Picciotto, M.M. Thackeray, Lithium insertion into spinel $LiFe_5O_8$, Mat. Res. Bull. 21 (1986) 583-592.