

Optimization of synthesis of single phase nanostructured LiFePO₄ materials

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Abstract: LiFePO₄ samples were first prepared by a modified sol - gel process and then the resulting LiFePO₄ xerogel was ground and calcined in a tube furnace in an inert atmosphere in nitrogen flow. The main goal of this research work which was lowering the temperature and the time of synthesis of LiFePO₄ was achieved. It was confirmed that the material contains only a LiFePO₄ triphylite phase and that the presence of carbon resulting from pyrolysis of initial carbonaceous reagents does not affect the crystalline structure of the material.

Key words: lithium iron phosphates, olivines, nanocrystalline materials, sol-gel preparation, thermal analysis, crystal structure

Optimalizacja procesu syntezy jednofazowych materiałów LiFePO₄ o nanometrycznych rozmiarach ziaren

Streszczenie: Próbkę materiału LiFePO₄ przygotowano zmodyfikowaną metodą zol - żel. Otrzymany kserożel został rozarty w młynku i kalcynowany w piecu rurowym w atmosferze ochronnej, w przepływie azotu. Główny cel pracy jakim było obniżenie temperatury i czasu trwania procesu, został osiągnięty. Potwierdzono, że materiał ten składa się tylko z tryfilitowej fazy LiFePO₄. Dowiedziono, że węgiel obecny w próbce, pochodzący z rozkładu pirolitycznego wyjściowych soli organicznych nie wpływa na formowanie się fazy krystalicznej.

Słowa kluczowe: fosforan litowo - żelazowy, oliwiny, materiały nanokrystaliczne, proces zol - żel, analiza termiczna, struktura krystaliczna

1. Introduction

The LiMXO₄ type compounds (M = Fe, Co, Ni; X = S, P, As, Mo, W) represent an intensively studied group of cathode materials for reversible lithium ion cells [1]. In 1997 the lithium iron phosphate LiFePO₄ with the olivine structure was recognized by Goodenough [2] as a prospective cathode material for Li-ion cells. Further studies confirmed the important advantages of LiFePO₄ over LiCoO₂ [3] used in commercial batteries. Those advantages include better safety, lower risk of explosion on overcharging, better thermal stability or lower cost of raw materials [4 - 5]. Unfortunately LiFePO₄ has a major drawback — poor electronic conductivity, 10⁻⁹ Scm⁻¹ at 20°C [6]. Many research works have been conducted to improve the conductivity of this material by several methods such as: aliovalent doping [7 - 8], preparation of composites with carbon [9], Fe₂P [10] or other additives [11], and modifications of grains morphology [12]. In the course of these studies it was shown that satisfactory performance of LiFePO₄ - olivine materials in batteries could be achieved if the average size of LiFePO₄ particles goes down to below 100 nm [13]. It was demonstrated that discharging

capacity drops with the increased particle sizes from 165 mAh/g for ~30-50 nm diameter to 72 mAh/g for 500 nm and bigger particles [13]. This feature also affects the conductivity in terms of the effective electrode resistance.

These days syntheses use either solid-state reaction or hydrothermal/solvothermal processes. In the first case the synthesis is typically conducted at temperatures above 700°C and may involve the synthesis from molten salts [14]. The advantages of the second example regard control of the homogeneity and the average crystallite size [15]. The conventional hydrothermal process requires a reaction time in range 5 - 12 h [16]. An important issue concerning cathode materials for Li - ion batteries is their cost, which should be as low as possible [17].

The aim of our work was to simplify and reduce the costs of LiFePO₄ preparation by lowering the temperature of the final syntheses and reducing the time of the overall processing. The prepared materials were studied by a number of methods: X-ray diffractometry (XRD), differential scanning calorimetry-thermogravimetry (DSC-TGA), scanning electron microscopy (SEM) and surface area (BET).

2. Experimental

2.1. Materials and synthesis

The material was prepared in accordance with a modified version of the sol-gel recipe described in [18]. We applied standard chemical procedure: organic salts of lithium acetate dihydrate (Sigma Aldrich, pure for analysis) and iron citrate monohydrate (Fluka, pure for analysis), dissolved separately in deionized water, and orthophosphoric acid (POCH, pure for analysis) as initial reagents. After the organic salts had dissolved completely the individual solutions were mixed together and orthophosphoric acid was added. The clear solution was continuously stirred at 80°C for a few hours and then 0.4 M of citric acid (POCH, pure for analysis) was added as complexing agent in the amount of 10 ml per for every 1g of final LiFePO_4 . The xerogel which was obtained after the initial evaporation of water was then dried at 150°C in air for 48 h, and finally ground in an agate mortar to a fine powder. The main modification was introduced in the calcination process. During a standard annealing process xerogels are synthesized at 700 - 800°C range for 6 - 8 h [19]. In our modified approach the temperature was lowered and the time was shortened to avoid uncontrollable agglomerates formation and to keep crystallites small during the prolonged thermal treatment. The xerogel was annealed for several hours in a steady flow of nitrogen in two stages: first at 300°C and then at 500°C for 5 h. The powder prepared in this way contained some amount of carbon, a residue of the decomposition of the complexing agent and organic salts.

2.2. Characterization

Thermal studies (DSC-TG) were carried out using a NETZSCH STA 449 F1 Jupiter apparatus in the range of 20 - 500°C at a 5°C min⁻¹ heating rate, on 25 mg samples. The phase composition of the samples was examined by powder X-ray diffractometry (XRD) using a Philips X'Pert apparatus equipped with Cu K α X-ray source with Ni filter ($\lambda = 1.54\text{\AA}$). The XRD measurements at a set of temperatures (30 - 800°C) were carried out using an Anton-Paar HTK1200 high-temperature oven chamber. Results were analyzed and confronted with the thermal features seen in DSC-TG traces of the same materials. The morphology of the powders was investigated by scanning electron microscopy (SEM) using a Cross Beam Auriga (Carl Zeiss) setup. Specific surface area was measured using QUADRASORB evoTM Gas Sorption Surface Area based on BET theory [20] at relative pressure conditions $P/P_0 = 0.05 - 0.3$, where P_0 – adsorbate saturated vapor pressure.

3. Results and discussion

DSC-TG curves of a xerogel are shown in Fig. 1. Measurements were taken in nitrogen atmosphere to prevent iron oxidation from Fe^{2+} to Fe^{3+} . Up to 350°C it is easy to see a single endothermic peak corresponding to the thermal decomposition of the organic components of citrates and acetates as well as the evaporation of residual water correlated with TG trace. An exothermic doublet above 400°C on DSC curve marks a two step

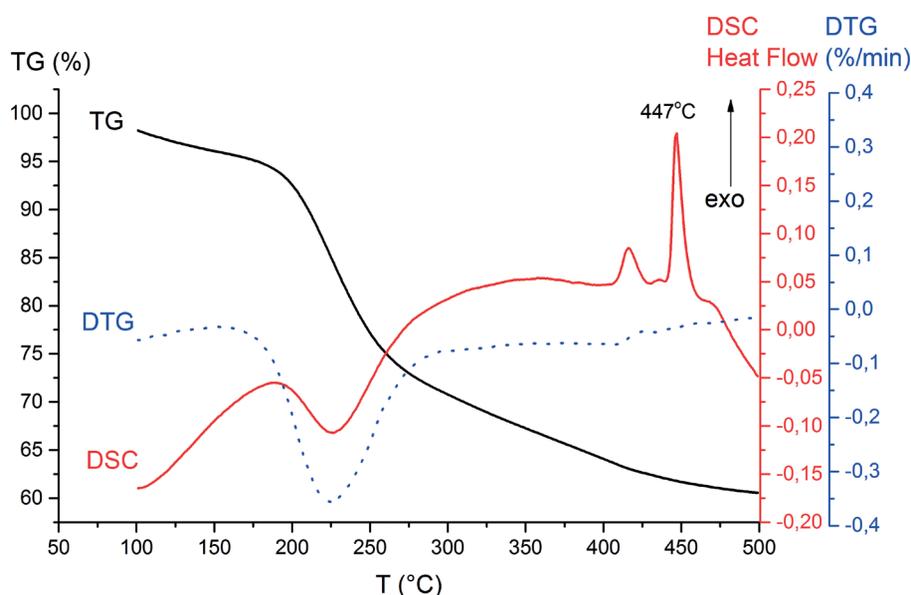


Fig. 1. Thermogram DSC/TG/DTG of a LiFePO_4 xerogel, heating rate 5°C/min in nitrogen atmosphere. DSC curve shows crystallization process during heat-treatment.

Rys. 1. Termogram DSC/TG/DTG kserożelu LiFePO_4 , szybkość grzania 5°C/min w atmosferze azotowej. Krzywa DSC pokazuje proces krystalizacji w czasie obróbki termicznej.

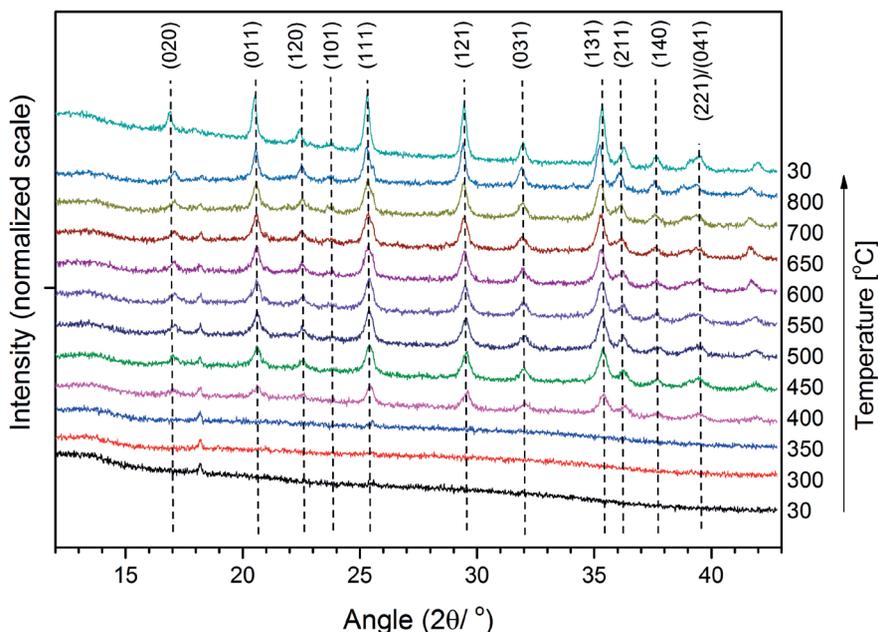


Fig. 2. Series of XRD patterns showing LiFePO_4 triphylite phase formation in function of temperature. The temperature sequence goes from in-situ measurements in nitrogen atmosphere. Eye catching dashed lines of LiFePO_4 reflections.

Rys. 2. Seria dyfraktogramów rentgenowskich XRD pokazujących proces formowania się fazy tryfilitowej w funkcji temperatury. Sygnał XRD zbierano w czasie trwania procesu wygrzewania. Przerwana linią zaznaczono miejsca występowania refleksów braggowskich dla fazy tryfilitowej LFP.

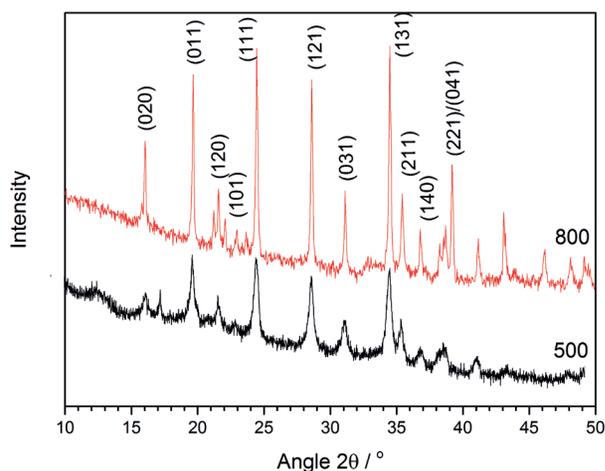


Fig. 3. XRD patterns for LiFePO_4 synthesized in nitrogen atmosphere at 500 and 800°C with indexed Bragg reflections of LiFePO_4 olivine from ICDD card no. 40 - 1499.

Rys. 3. Dyfraktogramy XRD LiFePO_4 syntetyzowane w temperaturze 500°C i 800°C z zaindeksowanymi refleksami braggowskimi zgodnymi z kartą ICDD nr 40 - 1499.

crystallization process of LiFePO_4 triphylite phase. Further structural investigations (XRD, Fig. 2) showed that a small exothermic feature around 420°C is not correlated with structural changes or formation of an additional phase. The calculated derivative of the original TG curve (DTG) depends on the temperature in an almost identical way as the measured DSC signal. The only difference which can be noted between DSC and DTG is the presence of an exothermic doublet in DSC (in the range of 410 - 450°C)

with no effect in DTG trace at the same temperature. The reasons of the presence of such doublet could be assigned to pre-formation of triphylite phase, formation of intermediate composition, such as LiH_2PO_4 [21], or thermal decomposition of lithium acetate [22].

The formation of triphylite phase was investigated by X-ray diffractometry. *In-situ* observations were conducted at a series of temperatures (300 - 800°C) in nitrogen atmosphere. Before these studies, xerogel was pre-heated in an inert atmosphere up to 300°C in order to perform the pyrolytic decomposition of organic salts and to remove its gaseous products. This temperature selection was based on the analysis of the endothermic features in the DSC curve. Fig. 2. presents a collection of XRD patterns. All Bragg reflections correspond to the orthorhombic LiFePO_4 triphylite phase (Pnma space group, ICDD card No. 40 - 1499) [23]. There are no peaks from unwanted phases like Fe_3P , Fe_2P , $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ or Fe_2O_3 . A small visible single peak at ca. 18° corresponds to the sample holder's material. This peak fades as intensity of triphylite phase reflections are increased during the calcination process.

The final high temperature XRD scan was performed at 800°C. After cooling down the last scan was collected at room temperature. The observed series of XRD patterns proved that the material is thermally stable in a wide range of temperatures in an inert atmosphere. More detailed results of studies on crystal structure of samples prepared at 500°C and 800°C are presented in Fig. 3. The positions of the Bragg reflections for both samples are identical, but the reflections for the material prepared at 500°C are much wider and less intense in comparison to

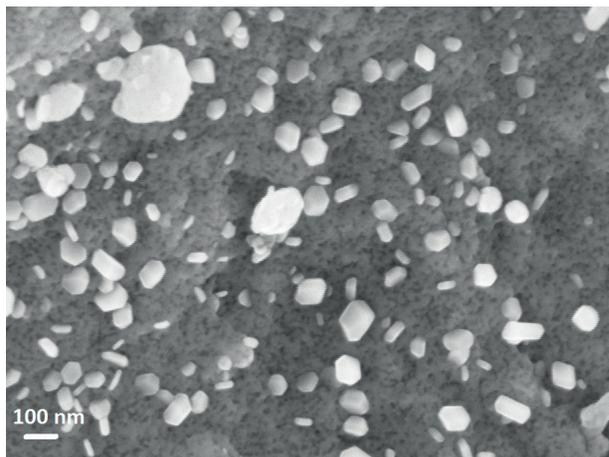


Fig. 4. SEM micrograph of nanostructured LiFePO_4 synthesized at 500°C in N_2 . Clearly visible nanosized hexagonal platelets of LiFePO_4 (white or light grey particles).

Rys. 4. Obraz SEM mikrostruktury LiFePO_4 po syntezy w 500°C w atmosferze azotowej. Widoczne na zdjęciu nanometryczne heksagonalne płytki (białe lub jasnoszare obiekty).

those for the material synthesized at 800°C . An average crystallite sizes estimated by the Scherrer formula [24] were 50 - 60 nm and 10-20 nm for LiFePO_4 calcined at 800°C and 500°C , respectively.

Detailed studies on thermal treatment of xerogel based on XRD and DSC measurements showed a small shift in triphylite formation's temperature. XRD patterns revealed that the main reflections of the LiFePO_4 phase appeared around 400°C , while with DSC scans the crystallization doublet was recorded at about 420°C . Probably this shift is due to the different heating protocols and rates between DSC and XRD experiments. The heating rate in DSC process was $5^\circ\text{C}/\text{min}$ and in various temperature XRD measurements it was around $0.5^\circ\text{C}/\text{min}$. In such case recording of DSC exothermic peak is delayed in time due to the inertness of the sample, which is manifested by an upward temperature shift. In our previous research [18] additional peak in lower temperature was not present in DSC scans because the starting materials used for the sol-gel synthesis were different. As temperature XRD measurements have shown there is no additional phase during heating process in the range of $400 - 450^\circ\text{C}$. This means that an additional peak in the DSC curve is related to the decomposition of acetates. Longer temperature exposure and the heating time during XRD measurements allowed triphylite phase formation and stabilization at lower temperature. Though One can the peaks visible in XRD patterns correspond to the triphylite phase, not all peaks are present. This may indicate that 400°C is the temperature high enough to initiate the process of crystallization, but too low to complete the phase conversion. Some amount of organic components may still be present in the sample which manifests itself by a relatively high noise to signal ratio.

In addition to the structural analyses, SEM observa-

tions were also conducted to the microstructure. Fig. 4. presents a micrograph of an as-received material synthesized at 500°C with well developed hexagonal platelets of LiFePO_4 [25], of diameters below 100 nm and heights about 15 - 20 nm. Those low values as well as crystallite size estimates from the Scherrer formula (10 - 20 nm), prove that the obtained samples are true nanostructural materials.

The specific surface area of a sample prepared at 500°C determined by the BET method was about $86 \pm 4 \text{ m}^2/\text{g}$, which is considerably higher than the values in range 11- 44 m^2/g reported in the literature [26 - 28].

4. Conclusions

The paper presents a modified approach to the preparation of nanostructured LiFePO_4 materials. It was shown that, using a modified sol-gel process and inexpensive reagents, the syntheses of LiFePO_4 olivines can be considerable improved by reducing their temperature from typical 800°C to ca 500°C and by reducing their time from 8 hrs to 5 hrs. As prepared material was nanostructural with particle size below 100 nm, as shown by SEM with crystallite sizes about 10 - 20 nm, calculated by the Scherrer formula. An increased specific surface area and a nanostructural character of the synthesized materials is of great advantageous for their application in lithium-ion batteries. Moreover the introduced synthesis modifications make the whole process more economical.

5. References

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