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$LiFePO_4$ AS AN ELECTRODE MATERIAL FOR LITHIUM-ION BATTERIES

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Lithium iron phosphate (LFP) samples have been synthesized by a solid-state method from Li_2CO_3, $(NH_4)_2HPO_4$, and $FeC_2O_4 \cdot 2H_2O$ in the presence of citric acid monohydrate as a source of carbon. It has been shown that LFP samples have initial capacity of 130 $mAh \cdot g^{-1}$ at a current rate of 0.6C.

There is an increasing claim for applications of electrochemical energy systems in energy storage, transportation and portable electronics, and a lot of electrode materials for lithium ion batteries have been created during last thirty years. Lithium ion phosphate (LFP) has been recommended as a cathode material in 1997 [1]. Since then, different methods of obtaining LFP have been used. This material has specific advantages and disadvantages. High theoretical capacity (170 $mAh \cdot g^{-1}$), thermal stability (up to 80 °C), high potential of charge/discharge (3.4V *vs* Li^+/Li) and a number of charge/discharge cycles (2000-8000) have been considered as advantages. Low electronic conductivity at the room temperature (10^{-9} $S \cdot см^{-1}$) and coefficient of diffusion ($1.8 \cdot 10^{-14}$ $см^2 \cdot с^{-1}$) can be estimated as disadvantages [2]. The properties of LFP obtained by different methods are summarized in Table 1. The highest discharge rates and capacities have been achieved for samples obtained by means of a rheological method. Spray pyrolysis and microwave synthesis give good results, particularly 59 $mAh \cdot g^{-1}$ at the scanning rate of 20C.

In this paper, LFP has been synthesized by the traditional solid-state method in the presence of citric acid monohydrate as a source of carbon, so as to ensure a conductive coverage of the LFP particles. The data on morphology and electrochemical properties of the sample obtained are presented and discussed.

Table 1. Physical-chemical and electrochemical characteristics of electrode materials obtained by different methods.

Method of synthesis	Precursors, carbon source	Temperature, atmosphere, regime of cycling	Discharge capacity $mAh \cdot g^{-1}$	Ref.
Rheological	H_3PO_4, $FeSO_4 \cdot 7H_2O$, $LiOH \cdot H_2O$, H_2O_2, starch	600°C (inert atmosphere), 2.0–4.4 V, 0.2–30C	157–72	[3]
Rheological	H_3PO_4, $FeSO_4 \cdot 7H_2O$, $LiOH \cdot H_2O$, H_2O_2 stearic acid	600°C (inert atmosphere), 2.0–4.4 V, 0.5–30C	160–93	[4]
Spray pyrolysis	Li_2CO_3, $Fe(NO_3)_3 \cdot 9H_2O$, $NH_4H_2PO_4$ citric acid	700°C (inert atmosphere), 2.0–4.2 V, 0.1–20C	159–60	[5]
Combined spray pyrolysis + “wet” treatment in a ball mill	$Li(HCOO) \cdot H_2O$, $FeCl_2 \cdot 4H_2O$, H_3PO_4	500 °C 600 °C 700 °C 800 °C (N_2 +3%H_2), 2.5–4.5 V, 0.1–20C	160-15 150-75 145-35 130-25	[6]
Microwave heating	$CH_3COOLi \cdot 2H_2O$, $FeSO_4$, H_3PO_4, citric acid, polyethylene glycol	400 Вт, 2.7–4.2 V, 0.2–20C	152–59	[7]

Research Methodology

Li_2CO_3, $(NH_4)_2HPO_4$, $FeC_2O_4 \cdot 2H_2O$ and citric acid monohydrate in respective amounts were mixed in a ball mill for 15-20 min. Pyrolysis and thermal treatment of the mixture were performed at 400 °C and 700 °C respectively. Working electrodes were made of 85% of the material under consideration, 7% of a conducting additive (carbon black) and 8% of a poly(vinylidene difluoride) binder. The slurry was homogenized by an ultrasonic disperser. It was needed for grinding the particles of the material and carbon black. After the removal of the solvent under an IR

radiator the quantity of LFP in a dried remainder was of 8-10 mg·cm^{-2}. The electrodes were rolled so as to decrease the thickness of the layer from 110-90 to 20-30 μm.

Electrochemical measurements were performed in model CR2016 coin cells on a home-made automated electrochemical workstation using cyclic voltammetry (CV) and galvanostatic charge/discharge cycling methods.

Results and Discussion

Cyclic voltammetry demonstrates intercalation/deintercalation peaks at 2.5-4.2 V. Galvanostatic tests reveal that the material obtained has discharge capacity of 130 mAh·g^{-1} and 90 mAh·g^{-1} at the current rates of 0.6C and 2C, respectively (Fig. 1). Such a low value of discharge capacity may be due to the fact that the decomposition process is not finished at the temperature chosen for annealing. As follows from micrographs (Fig. 2), the remnants of citric acid are not burnt completely.

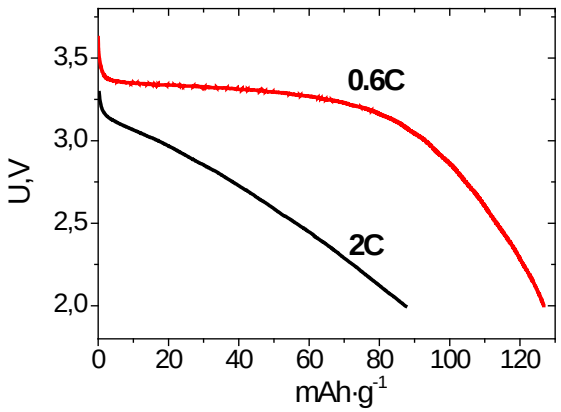

***Figure 1**. Discharge capacities of LFP samples at different current rates*

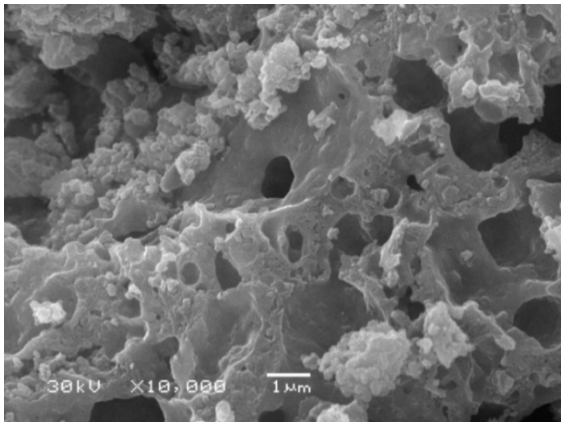

***Figure 2**. A micrograph of LFP samples*

Conclusions

Lithium iron phosphate (LFP) samples synthesized by a solid-state method demonstrate initial capacity of 130 $mAh \cdot g^{-1}$ at a current rate of 0.6C and discharge capacity of 90 $mAh \cdot g^{-1}$ at a current rate of 2C.

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