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SYNTHESIS AND PROPERTIES OF NANOPARTICLES BASED ON C/Fe₃O₄, C/Fe_{3-x}Cr_xO₄, C/Li_{0.5}Fe_{1.5}CrO₄ – ANODE MATERIALS FOR LITHIUM-ION BATTERIES

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High charging potential of Fe₃O₄ (1.75 V), its low conductivity and significant changes of volume during charging/discharging are main disadvantages that prevent commercialization of this material as an active constituent of anode for lithium-ion batteries. Various ways for minimization of these drawbacks are discussed. It is suggested that the necessary functional properties of the anode material can be formed directly during the synthesis process. A number of composites, such as C/Fe₃O₄, C/Fe_{3-x}Cr_xO₄, C/Li_{0.5}Fe_{1.5}CrO₄, have been obtained using the Pechini method. Modification of the synthesis technique has been developed. Phase composition and morphology of powders were studied by XRD, SEM and EDX analysis. It has been found that the products of synthesis of Fe₃O₄, Fe₂CrO₄, Li_{0.5}Fe_{1.5}CrO₄ are characterized by good crystallinity, the average size of powder crystals is 29 (Fe₃O₄), 12 (Fe₂CrO₄) and 18 nm (Li_{0.5}Fe_{1.5}CrO₄). Cyclic voltammograms (CV) and galvanostatic charging/discharging curves were obtained within the potential region from 0.05 to 2.0 V (Li⁺/Li), the scan rate was 0.1 mV/s. The C/Fe₃O₄ composite has been found to show high reversible capacitance for the first cycle (~1000 mAh/g) at high C/10 current. At C/10, the C/Fe₂CrO₄ anode shows the capacitance of ~900 mAh/g for the 1st cycle. At the same time, the charging capacitance decreases from 1.8 to 1.1 V. Doping with chromium and lithium leads to decrease of charging potential from ~1.8 V (C/Fe₃O₄) down to 0.9 V (C/Li_{0.5}Fe_{1.5}CrO₄). Decrease of grain size down to 10–30 nm and conducting carbon on the grain surface provide better kinetics of the charging/discharging processes. This approach allows us to reach reversible capacitance of ~800 mAh/g for the best material (C/LiFeCrO₄). This characteristic is achieved in the first cycle of charging/discharging at C/10.

Keywords: doped Fe₃O₄, anode, electrochemical properties, lithium-ion batteries

INTRODUCTION

The growing demand for efficient energy conservation systems creates an increasing interest in the chemistry of high-energy sources, dominated by lithium-ion batteries (Li-ion). Graphites with a low theoretical capacity of 372 mAh/g are used as anode material in commercial LIB. It is possible to replace them with materials with a larger capacity on the basis of transition metal oxides. To this end, the anodes of Co, Ni, Fe, Cu oxides are widely studied [1]. Among of them, the most promising material is Fe₃O₄, due to its low cost, environmental friendliness, electrical conductivity, which is better than that of other oxides and high charging capacity (1000 mAh/g) [2]. In contrast to graphite, when intercalation / deintercalation of lithium occurs in this anode,

the current-forming reaction is the reaction of electrochemical conversion, which occurs according to the scheme:



The extraction of lithium ions from Li₂O in the charge process (2FeO+2Li₂O↔2FeO+4Li⁺+4e⁻) proceeds rather slowly, making the whole process in the anode partially irreversible. The result is the high charge potential of Fe₃O₄, E_{ch} = 1.75 V (by Li⁺/Li) [2]. One more disadvantages of the Fe₃O₄ anode are low conductivity, significant changes in volume during charge/discharge. The last two shortcomings lead to a slow kinetics of the conversion reaction, the agglomeration of Fe₃O₄ in the film, even to a partial loss of adhesion to the substrate. All these disadvantages of Fe₃O₄ as anode material substantially complicate its

commercial use. Various ways to minimize these shortcomings that are possible in the synthesis of anode material have been discussed in the publications. Thus, reducing the size of Fe_3O_4 crystals reduces the path to lithium diffusion, improving the kinetics of reciprocal accumulation and preservation of lithium. Hybridization, the optimal morphology of Fe_3O_4 particles with nano-carbon may improve the electron transfer, and in the case of the formation of the “shell-nucleus” structure, a buffer is required to change the Fe_3O_4 volume and thus maintain the stability of the cycling of Fe_3O_4 [1–3]. The material of Cr_2O_3 has a rather low charging potential but very low conductivity [4–5] and is therefore also unsuitable for practical use.

In this paper, the possibility of improving the characteristics of anode material, which was created from a solid solution of Cr_2O_3 in Fe_3O_4 , its nanocrystals have a carbon coating has been studied. According to our methodology, synthesized nanocrystalline samples Fe_3O_4 , $Fe_{3-x}Cr_xO_4$, $Li_{0.5}Fe_{1.5}CrO_4$ and their carbon composites obtained by pyrolysis of tartaric acid at 220 °C have been synthesized. Its charging potentials, charge capacities and cyclic stability have also been studied.

SYNTHESIS

The synthesis of the compounds Fe_3O_4 , Fe_2CrO_4 and $Li_{0.5}Fe_{1.5}CrO_4$ was performed by Pechini method with some our modifications. Li_2CO_3 , $Cr(NO_3)_3 \cdot 6H_2O$, iron(II) gluconate, ethylene glycol, citric acid have been used as precursors. Precursors were homogenized in the mixture of citric acid and ethylene glycol at 85 °C for 2 h, a calculated amount of oxidant NH_4NO_3 was injected into the melt and temperature was risen to 120 °C for obtaining of the required ratio Fe^{3+}/Fe^{2+} in Fe_3O_4 synthesized and oxidation of the organic matrix. Then the temperature of the reaction medium was increased to 150 °C and the obtained mixture was kept under vigorous stirring for 2 h, then the temperature was adjusted to 200 °C to spontaneous burning of mixture. The washed and dried synthesis product was annealed at 600 °C (in the case of Fe_3O_4 and Fe_2CrO_4) or at 650 °C (in the case of $Li_{0.5}Fe_{1.5}CrO_4$) under argon atmosphere for 4 h.

CHARACTERIZATION OF SYNTHESIS PRODUCTS AND TESTING THEM AS ANODIC MATERIALS

The phase composition, morphology of Fe_3O_4 , Fe_2CrO_4 , $Li_{0.5}Fe_{1.5}CrO_4$ powders were identified by the methods of X-ray diffraction (XRD, DRON-4M, CuK_{α} -radiation), electron microscopy (SEM, JSM-microscope 6060LA JEOL) was performed and elemental composition was identified with EDX-analysis spectrometer JED 2300, the average size of the particles d was calculated using the Sherer formula.

Anodic mass made of this powders has the following composition: synthesis product (80 wt. %), PVDF (polyvinylidene difluoride) solution in 1-methyl-2-pyrrolidone (10 wt. %), acetylene black (10 wt. %). Thick film electrodes were formed on substrates from stainless steel (mesh) by technology for the preparation of anode paste.

Electrodes after drying in a vacuum at 120 °C were tested in a cell with Li counter electrode (it also serves as reference electrode), a separator of porous polypropylene, an electrolytic solution of 0.6 M lithium bis (oxalate) borate (LiBOB) in equimolar mixture with ethylene carbonate (EC) and dimethyl carbonate (DMC) with clamping current leads of stainless steel. The cell was assembled in a dry box in an atmosphere of argon. Cyclic voltammograms (CV) and galvanostatic charge/discharge characteristics were measured filmed using potentiostates (IPC Compact, Elins P-2X). The measurements were performed in the potential region from 0.05 to 2.0 V (Li^+/Li) at the rate of 0.1 mV/s.

DISCUSSION OF RESULTS

According to the XRD (Fig. 1), the products of the synthesis of Fe_3O_4 , Fe_2CrO_4 , $Li_{0.5}Fe_{1.5}CrO_4$ have good crystallinity, all the reflections in Fig. 1 correspond to planes (220), (311), (400), (422), (511), (440), (533), which corresponds to the spinel structure of Fe_3O_4 and are consistent with JCPDS No: 00-11-0614). For peak (311), the calculated average size of synthesized powder crystals is 29 nm (Fe_3O_4), 12 nm (Fe_2CrO_4), 18 nm ($Li_{0.5}Fe_{1.5}CrO_4$).

According to the SEM image, the cubic nanocrystals of $Li_{0.5}Fe_{1.5}CrO_4$ are strongly agglomerated and consist of blocks with the size of 1 micron (see Fig. 2).

For anodic material in the form of nanocomposite with carbon of single-phase Fe_3O_4 oxide with an average grain size of 29 nm, charge/discharge characteristics and charge stability have been investigated during cycling (Fig. 3).

The material $\text{C}/\text{Fe}_3\text{O}_4$ showed a high reversible capacity of the first cycle (~ 1000 mAh/g) at high $\text{C}/10$ current. However, the average charge potential is a sufficiently high $E_{\text{ch}} \sim 1.8$ V (Li/Li + electrode), which makes commercial use of such anode inappropriate, since for commercial graphite anodes the value of E_{ch} does not exceed 0.5 V. The anode of pure $\text{C}/\text{Cr}_2\text{O}_3$ has low rather (1.1 V) charge potential, but a low conductivity [4–5]. Therefore, it would

be useful to evaluate the characteristics of a compromise anodic material, such as $\text{C}/\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$, obtained by the partial replacement of iron by chromium in a magnetite lattice. At the same time, the problem of compensating the change of the anode volume during cycling is solved partly due to the difference in the values of the charge potential for the $\text{C}/\text{Fe}_3\text{O}_4$ and $\text{C}/\text{Cr}_2\text{O}_3$ anodes. As the maximum allowable concentration of $\text{C}/\text{Cr}_2\text{O}_3$ in $\text{C}/\text{Fe}_3\text{O}_4$, the x value was adopted which still retains the cycling reversibility of all investigated materials it corresponds to the material $\text{C}/\text{Fe}_2\text{CrO}_4$. At $\text{C}/10$, anode $\text{C}/\text{Fe}_2\text{CrO}_4$ anode showed a capacity of the 1st cycle ~ 900 mAh/g. At the same time, the charge capacity E_{ch} decreased from 1.8 to 1.1 V.

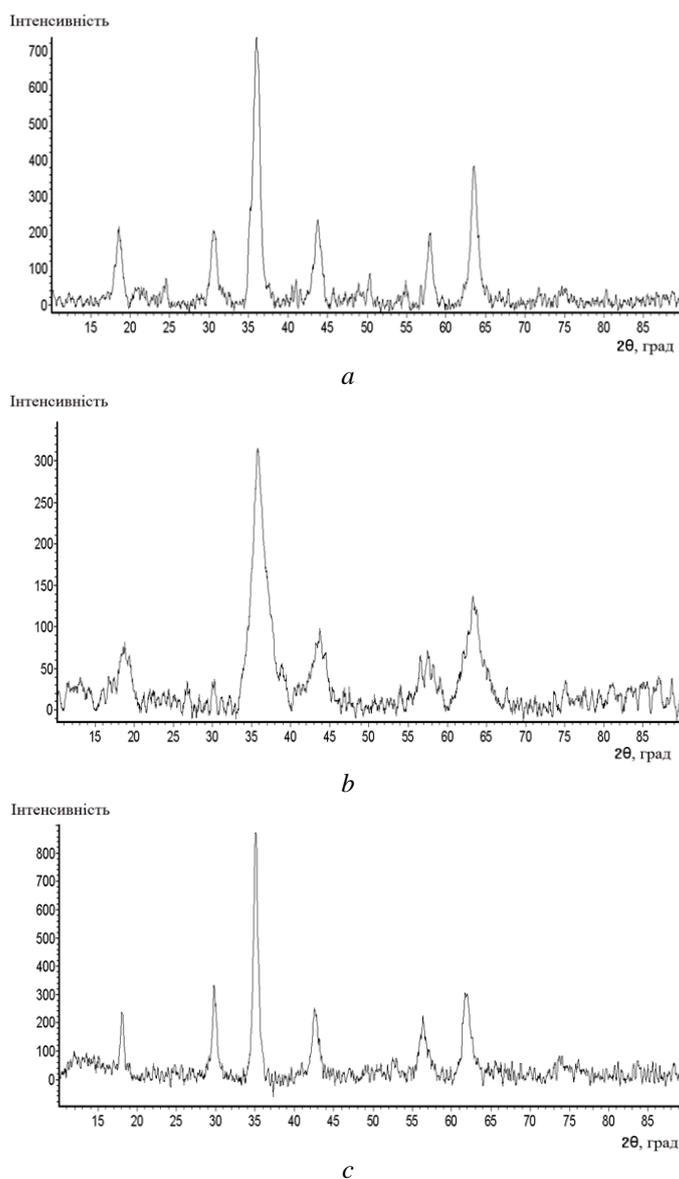


Fig. 1. XRD patterns of the synthesized particles of $\text{Li}_{0.5}\text{Fe}_{1.5}\text{CrO}_4$ (a), Fe_2CrO_4 (b), Fe_3O_4 (c)

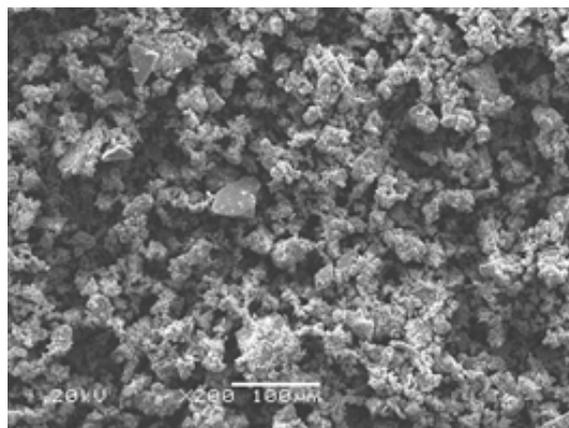


Fig. 2. SEM image of the synthesized $Li_{0.5}Fe_{1.5}CrO_4$ powder

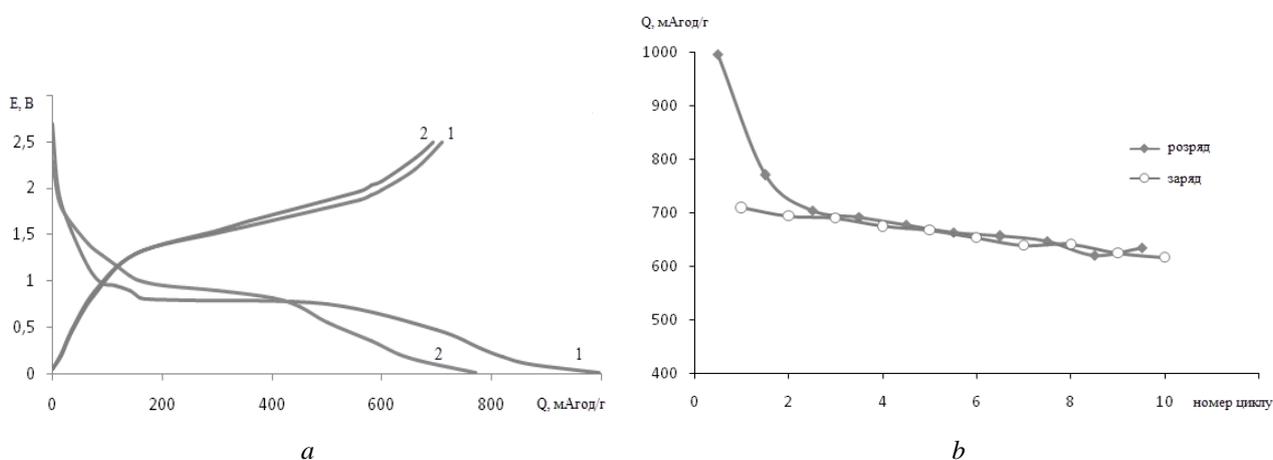


Fig. 3. Electrochemical characteristics of the electrode C/Fe_3O_4 : galvanostatic charge-discharge curves for the first two cycles (1,2 cycle number), at potentials of 0.05–2.0 V, current $C/10$ (a), change of the electrode charge during cycling within 10 cycles, current $C/10$ (b)

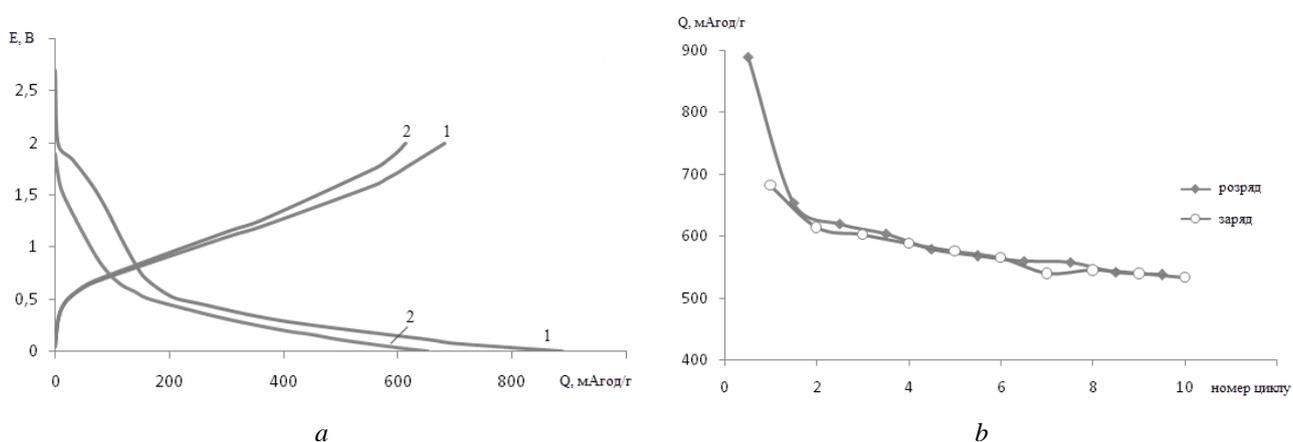


Fig. 4. Electrochemical characteristics of the electrode C/Fe_2CrO_4 : galvanostatic charge-discharge curves for the first two cycles (1,2 cycle number), at potentials of 0.05–2.0 V, current $C/10$ (a), change of electrode charge during cycling within 10 cycles, current $C/10$ (b)

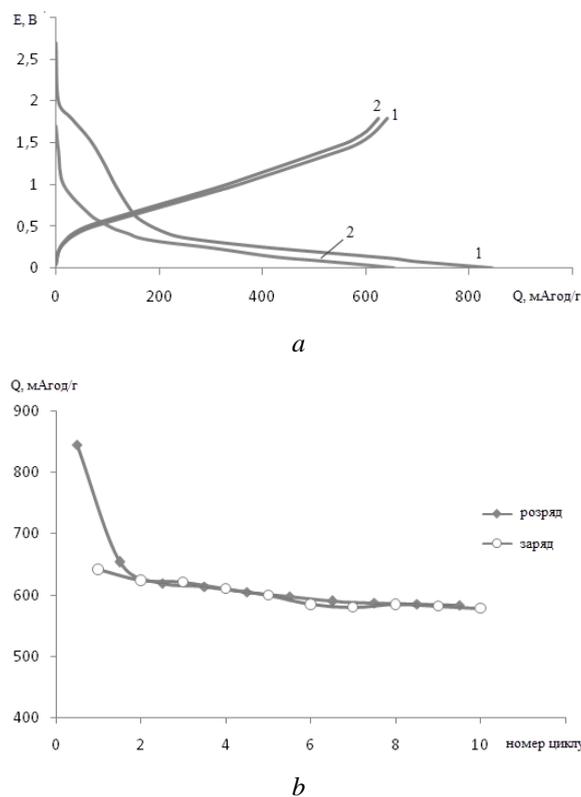


Fig. 5. Electrochemical characteristics of the electrode $C/Li_{0.5}Fe_{1.5}CrO_4$: galvanostatic charge-discharge curves for the first two cycles (1,2 cycle number), at potentials of 0.05–2.0 V, current $C/10$ (a), change in charge of the electrode during cycling within 10 cycles, current $C/10$ (b)

Important properties of the synthesized anode material are indicated of change in charging potential when doping it with lithium in the process of synthesis. The charging potential of such material (Fig. 5) have been reduced to $E_{ch} \sim 0.9$ V with retaining its capacity during cycling at the level of 600 mAh/g.

The obtained result allows to hope that the optimization of the conditions for the synthesis of the material $C/LiFe_{3-x}Cr_xO_4$, in particular the formation of effective morphology, as found in [6–7] for C/Fe_3O_4 , will make it possible to approximate such anode to graphite at specific power with retaining its charging capacity.

CONCLUSIONS

According to the results of the study of synthesized samples of Fe_3O_4 , Fe_2CrO_4 , $Li_{0.5}Fe_{1.5}CrO_4$, it is possible to draw preliminary conclusions. Synthesis according to the modified Pechini scheme allows one to obtain nanocrystals of magnetite Fe_3O_4 and its doped forms. The anodic material in the form of a nanocrystalline phase of C/Fe_3O_4 has no commercial prospect because of the too high charging potential (1.8 V compared to 0.5 V for graphite). It is expedient to develop an optimal method for the synthesis of nanocrystals of $Li_{0.5}Fe_{1.5}CrO_4$ with the optimal morphology for the introduction/extraction of lithium.

Синтез та властивості наночасток на основі C/Fe₃O₄, C/Fe_{3-x}Cr_xO₄, C/Li_{0.5}Fe_{1.5}CrO₄ – матеріалу анодів для літій-іонних батарей

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Композити (C/Fe₃O₄, C/Fe_{3-x}Cr_xO₄, C/Li_{0.5}Fe_{1.5}CrO₄) синтезовані модифікованим методом Печіні. Допування магнетиту хромом і літєм приводить до зниження потенціалу заряду з ~1.8 В (C/Fe₃O₄) до 0.9 В (C/Li_{0.5}Fe_{1.5}CrO₄). Зменшення розміру зерна анодного матеріалу до 10–30 нм і присутність на поверхні зерна провідного вуглецю покращує кінетику процесів заряд/разряду, для кращого матеріалу (C/Li_{0.5}Fe_{1.5}CrO₄) дозволяє отримати зворотню ємність у першому циклі ~800 мАчас/г при струмі C/10.

Ключові слова: допований Fe₃O₄, анод, електрохімічні властивості, літій-іонні батареї

Синтез и свойства наночастиц на основе C/Fe₃O₄, C/Fe_{3-x}Cr_xO₄, C/Li_{0.5}Fe_{1.5}CrO₄ – материала анодов для литий-ионных батарей

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Композиты (C/Fe₃O₄, C/Fe_{3-x}Cr_xO₄, C/Li_{0.5}Fe_{1.5}CrO₄) синтезированы модифицированным методом Печини. Допирование магнетита хромом и литием приводит к снижению потенциала заряда с ~1.8 В (C/Fe₃O₄) до 0.9 В (C/LiFeCrO₄). Уменьшение размера зерна анодного материала до 10–30 нм и присутствие на поверхности зерна проводящего углерода улучшает кинетику процессов заряд/разряда, для лучшего материала (C/LiFeCrO₄) позволяет получить обратимую ёмкость в первом цикле ~800 мАчас/г при токе C/10.

Ключевые слова: допированный Fe₃O₄, анод, электрохимические свойства, литий-ионные батареи

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