Electrochemical Properties of Mesoporous γ-Fe$_2$O$_3$ Synthesized by Sol-gel Citrate Method

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Mesoporous γ-Fe$_2$O$_3$ was synthesized by sol-gel citrate method and investigated as a cathode material for lithium power sources. The values of the specific energy are equal to 200 W·h/kg for the discharge current of 1.0C that corresponds to real operating conditions of lithium power sources. Two kinetic processes take place at the discharge of lithium power sources. The first stage corresponds to the accumulation of Li$^+$ ions on the surface of the cathode material/electrolyte interface during discharge of lithium power sources. The accumulation of charge on the cathode material/electrolyte interface is accompanied by the percolation diffusion of Li$^+$ ions on the surface. The second stage corresponds to the diffusion of Li$^+$ ions in the crystal structure of the cathode material. The diffusion coefficients of lithium in the cathode material at different stages of the discharge process are calculated.

Keywords: Mesoporous γ-Fe$_2$O$_3$, Lithium power source, Specific surface area, Diffusion.

1. INTRODUCTION

One of the current problems of modern electrochemical power engineering is the approbation of nanostructured binary compounds of 3d-transition metals M$_m$X$_n$ (where M = Co, Fe, Ni, Cu; X = F, O, S, N) as cathode materials in lithium power sources (LPS). The potential benefits of such systems are their phase stability at the intercalation/deintercalation of Li$^+$ ions during the LPS cycling and high value of the specific characteristics at discharge (specific discharge capacity > 700 A·h/kg) [1].

The possibility to use iron oxides as a cathode material of LPS was firstly considered by the authors of [2]. The difficulties appearing in this case are associated, first of all, with irreversible phase transitions of the material with the introduction of lithium, small value of the diffusion coefficient of Li$^+$ ions, formation of a passivating film on the electrode surface, and significant changes in the material structure during intercalation that causes mechanical destruction of the electrode. The use of nanodispersed iron oxides is the effective way to solve these problems [3]. In particular, the prospects of application of nanodispersed γ-Fe$_2$O$_3$ as a cathode material of LPS attract more and more attention of researchers due to the presence in the defect spinel structure of the material of octahedral cavities suitable for the introduction of Li$^+$ ions. Thus, the authors of [4] established that for LPS with the cathode based on nanodispersed γ-Fe$_2$O$_3$ after the first cycle of intercalation/deintercalation (voltage range is 0.1-3.0 V, discharge current for the first two cycles is 45 A/kg, for the next ones – 500 A/kg) the value of the specific capacity is equal to 1032 A·h/kg and after the 50-th cycle – 224 A·h/kg.

The possibility to use mesoporous γ-Fe$_2$O$_3$ as a cathode material of LPS is promising, since morphology of this material allows to maximally fill positions suitable for localization of Li$^+$ ions that provides the correlation between the specific surface area of the cathode material and capacity characteristics of LPS. At that, the questions of establishing stability conditions of the crystal lattice and localization position of Li$^+$ cations at intercalation and study of the influence of the specific surface area and particles size on the discharge process of the electrochemical cell remain important.

Thus, the aim of this work was to establish the interrelation between the structural, morphological characteristics of mesoporous γ-Fe$_2$O$_3$ obtained by sol-gel citrate method and the electrochemical processes in LPS with the cathode based on the synthesized materials.

2. PRODUCTION OF THE MATERIALS AND METHODS OF THEIR STUDY

Mesoporous γ-Fe$_2$O$_3$ was synthesized by sol-gel citrate method, which provided, in our case, the mixing of 0.3 M of aqueous solutions of iron nitrate and citric acid and formation of a sol of iron citrate. The polymer xerogel of iron citrate formed due to evaporation of excess water was annealed at the temperature of 200 °C during 1.5 h that caused the formation of the iron oxide phase.

The diffractometer Rigaku D/Max 2200 PC Ultima III (CuK$_\alpha$-radiation) was used for the analysis of the phase composition and crystal structure of the synthesized materials. Information about the morphological characteristics of the synthesized materials was obtained by the nitrogen adsorption method on the sorbometer Quantachrome Autosorb Nova 2200e.

The investigation of the electrochemical properties of the synthesized mesoporous γ-Fe$_2$O$_3$ was performed using a two-electrode cell. The cathode mixture was prepared by mixing the synthesized material with acetylene soot and the binding additive (polyvinylidene fluoride) in the following ratio: γ-Fe$_2$O$_3$: acetylene soot : polyvinylidene fluoride = 80 : 15 : 5 (%). Metallic lithium served as the anode. 1 M solution of LiBF$_4$ in γ-butyrolactone acted as the electrolyte. The study of the electrochemical processes during the LPS discharge was carried out using the impedance spectrometer Autolab / Pgstat 12 in the gal-

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vanostatic mode in the voltage range of 3.2-0.5 V. The discharge occurred for the discharge currents of 1.0 C, 0.5 C, 0.1 C and 0.05 C and temperature of 25 °C. For a quantitative description of the intercalation process, the following parameter was applied: degree of implementation *X*, which is equal to the number of moles of Li^+ ions transferred through the electrolyte to the cathode at discharge in terms of 1 mole of the cathode material:

$$X = \frac{M}{m} \cdot \frac{It}{F}, \qquad (1)$$

where *I* is the current strength under the condition of galvanostatic discharge/charge during time *t*, *m* is the mass of the cathode material with molar mass *M*, *F* is the Faraday number.

3. RESULTS AND DISCUSSION

Based on the data of the X-ray analysis, the ultra-dispersed γ-Fe$_2$O$_3$ phase (Fig. 1) is formed as a result of annealing of the X-ray amorphous xerogel of iron citrate hydrate at the temperature of 200 °C in air. The average sizes of the coherent scattering regions calculated by the Scherrer formula are equal to 7-8 nm.

The specific surface area of the synthesized mesoporous γ-Fe$_2$O$_3$ was calculated by the Brunauer-Emmett-Teller (BET) method and is equal to 164 m^2/g. At that, mesopores of the diameter of 3-7 nm with the maximum in the vicinity of 5 nm (Fig. 2) make the main contribution to the volume of pores. One can also select pores of the size of 2 nm.
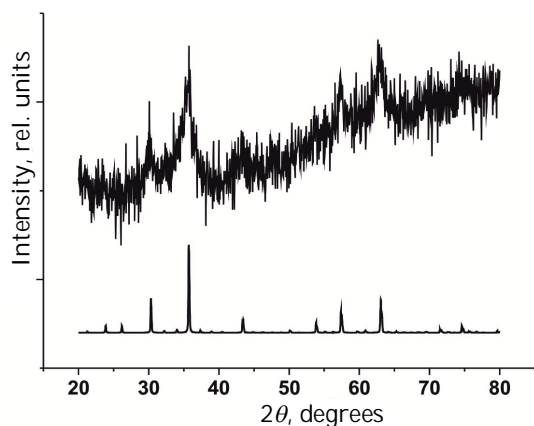

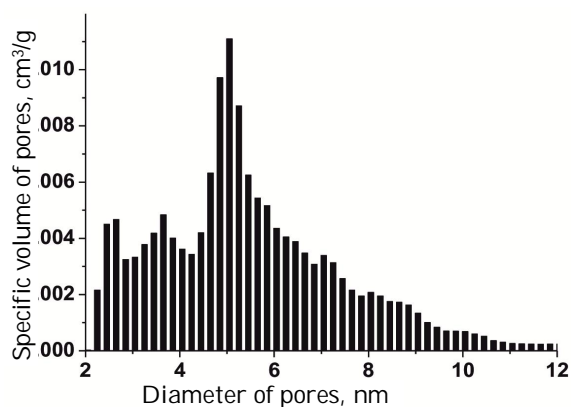Fig. 1 – Diffraction patterns of the synthesized mesoporous and reference (*ICSD* #35643) γ-Fe$_2$O$_3$

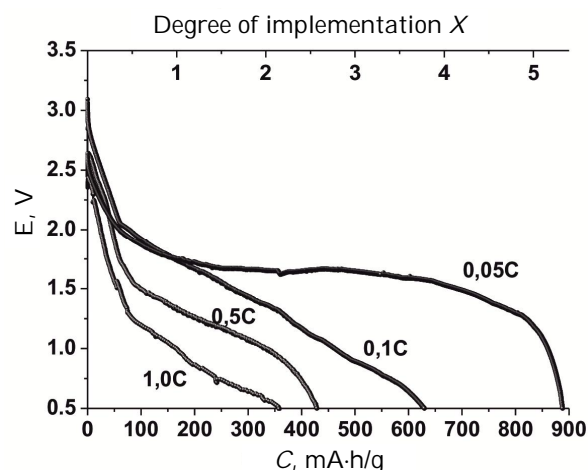Fig. 2 – Distribution of pores in sizes of the mesoporous γ-Fe$_2$O$_3$ synthesized by sol-gel citrate method

Fig. 3 – Galvanostatic curves of LPS with the cathode based on the mesoporous γ-Fe$_2$O$_3$ at different discharge modes

The discharge curves of LPS breadboard model with the cathodes based on the mesoporous γ-Fe$_2$O$_3$ for the values of the discharge current of 1.0 C, 0.5 C, 0.1 C, and 0.05 C are illustrated in Fig. 3. The maximum value of the specific discharge capacity for LPS is equal to 890 mA·h/g at the current of 0.05 C. Moreover, for this discharge current there is a typical plateau on the galvanostatic curve at the voltage of about 1.6 V corresponding to the reaction of irreversible transformation of the defect spinel structure of γ-Fe$_2$O$_3$ into the structure of mine salt [5]. With increasing discharge current, specific capacity of LPS decays reaching the value of 360 mA·h/g at the current of 1.0 C.

The data obtained from the comparison of the integral specific energy characteristics, in particular, the specific energy emitted in the LPS discharge ($W = \int IU(G) dG/mt$), supplements previous results of the electrochemical studies of mesoporous γ-Fe$_2$O$_3$. It is established that at the discharge current of 1.0 C, the specific energy of LPS is equal to 200 mW·h/g that corresponds to real operation conditions of LPS.

Moreover, synthesized mesoporous γ-Fe$_2$O$_3$ was also tested in the galvanostatic charge/discharge mode in the voltage range of 3.2-1.6 V at the current of 0.1 C. For several initial cycles, specific discharge capacity of LPS varies slightly being in the vicinity of 250 mA·h/g (see Fig. 4). After the 5th cycle, there is a sharp decrease in the specific discharge capacity of the material and after

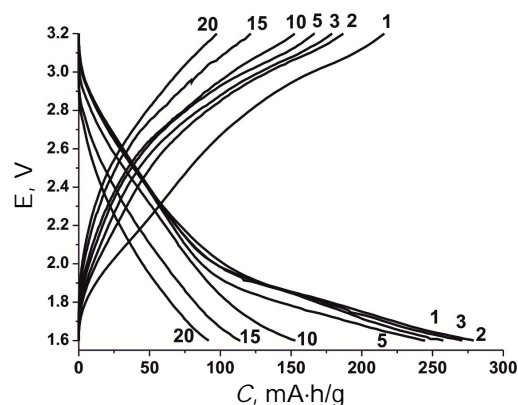
Fig. 4 – Charge/discharge curves for LPS with the cathode based on mesoporous γ-Fe$_2$O$_3$ at the current of 0.1 C

the 20th cycle capacity is equal to 93 mA·h/g. Coulomb efficiency of the charge/discharge processes depends non-linearly on the number of cycle reaching the maximum value of 57 % for the 3*d* cycle.

The theory of sub-potential deposition was used for the description of the intercalation process of Li$^+$ ions to the structure of mesoporous γ-Fe$_2$O$_3$ in discharge of LPS. This theory provides for electrostimulated adsorption of charge carriers on the cathode material surface at potentials lower than the Nernst equilibrium potential of this metal cation recovery. In this case, the model of Frumkin adsorption isotherm can be applied for the description of the intercalation process in the presence of interaction between intercalated particles [6]. For the process of sub-potential deposition at arbitrary filling of surface positions, the presence of the interaction between deposited cations and percolation diffusion of charge carriers over the surface positions, the Nernst equation can be written in the following form:

$$E(x) = E^0 - \frac{RT}{F} \cdot \ln \frac{x}{1-x} - \frac{RT}{F} \cdot xg - \frac{P}{x}, \qquad (2)$$

where E is the electrode potential, E^0 is the standard electrode potential, R is the universal gas constant, T is the temperature, P is the energy loss by overcoming the cohesive attractive forces between layers of the material, g is the parameter describing the interaction.

Positive values $g > 0$ correspond to repulsion between the particles, $g = 0$ determines the absence of the interaction, negative values $g < 0$ correspond to attraction between the particles; at that, the process velocity reaches the maximum value at $g = -4$ indicating the formation of a new phase.

By differentiating equation (1), we obtain the functional dependence of the potential change on the change of the degree of implementation dE/dx:

$$\frac{\partial \left(E - E^0 \right)}{\partial x} = -\frac{RT}{F} \cdot \left[g + \frac{1}{x \left(x_{\max} - x \right)} \right], \qquad (3)$$

where $x_{\max}$ is the maximum number of moles of lithium passed through the electrolyte during discharge.

Using the experimental discharge curves (Fig. 3 and Fig. 4), we plotted the dependences dE/dx, which were well approximated by the functions (3) (see Fig. 5). It is revealed that in our case $g > 0$ (Fig. 5a) that corresponds to the Coulomb repulsion between charge carriers. On all dependences $dE/dx(x)$, the presence of two stages is fixed, and the transition between these stages occurs in the vicinity of values $x_{cr} = 0.4$-0.5. Increase in the discharge current leads to the increase of g, i.e. the growth of the repulsion rate between Li$^+$ ions. It is important that with increasing number of the cycle, decrease in the contribution of the second stage into the dependence dE/dx is fixed in the galvanostatic cycling mode for insignificant changes for the first stage (Fig. 5b).

In view of the above findings that dependence dE/dx for all studied systems is well described by the Frumkin adsorption isotherm, one can propose the following explanation of the presence of two stages of changing dE/dx. Probably, the first stage corresponds to accumulation of Li$^+$ ions on the surface of the cathode material/electrolyte interface during LPS discharge, and for values of
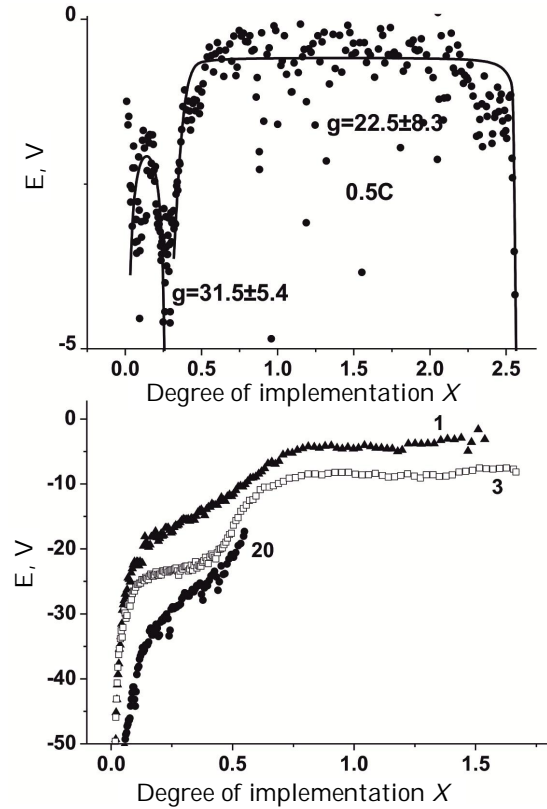

Fig. 5 – Dependences dE/dx for LPS with the cathodes based on mesoporous γ-Fe$_2$O$_3$ for the discharge current of 0.5 C (a) and in the case of galvanostatic cycling at the discharge current of 0.1 C (b)

$x \le 0.4$-0.5 the accumulation process is reversible. The second stage corresponds to the introduction of Li$^+$ ions into the channels of the crystal lattice of the cathode material, at that after the 5th cycle efficiency of Li$^+$ ion extraction from the lattice sharply decreases, and after the 20th cycle – exclusively surface positions of lithium immobilization in the material operate only.

Kinetics of Li$^+$ ions introduction into the structure of mesoporous γ-Fe$_2$O$_3$ during LPS discharge was studied by the impedance spectroscopy method. The Nyquist diagrams are characterized by the presence of high-frequency deformed semicircle that provides the Faraday processes and low-frequency part, which describes the diffusion charge transfer process. The diffusion impedance is represented in the form of the Warburg impedance Z_W. The value of the Warburg coefficient σ was calculated by the slope of the linear part of the dependences of the impedance real component ReZ on $\omega^{-1/2}$. In the range of low frequencies, the intercalation process is described by semi-infinite diffusion, at that, the diffusion coefficient D_{Li} of Li$^+$ ions is calculated from the expression

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_{Li} D_{Li}^{0.5}} \right), \qquad (3)$$

where C_{Li} is the concentration of Li$^+$ions, which are transferred through the electrolyte and introduced into the structure of the cathode material or located on its surface [mole/cm^3], A is the geometric area of the electrode, n is the number of elementary charges transferred by the cation, σ is the Warburg coefficient.
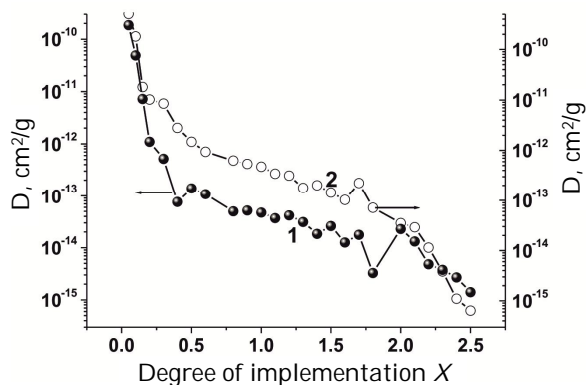
Fig. 6 – Dependence of the diffusion coefficients of Li$^+$ ions into the structure of mesoporous γ-Fe$_2$O$_3$ on the degree of implementation x

It is established that two kinetic processes are observed during the LPS discharge (Fig. 6). This agrees with the assumption of the Li$^+$ ion adsorption on the cathode surface and the intercalation into the material structure. Li$^+$ ions are accumulated on the surface and then migrate deep into the lattice, and their place is occupied by the next ions from the electrolyte. Charge accumulation on the surface of the cathode material/electrolyte interface is accompanied by the percolation diffusion of Li$^+$ ions. Filling of the channels for the degree of implementation $x \leq 0.4$ leads to a sharp reduction of the volume diffusion coefficient (curve 1, Fig. 6) in the range of 10^{-10}-10^{-13} cm^2/s. At the same time, the percolation diffusion coefficient decreases in the range of 10^{-10}-10^{-12} cm^2/s (curve 2, Fig. 6). After filling the surface at $x \approx 0.4$ there is a decrease in the rate of both processes with the corresponding decay of the kinetic coefficients and decrease in the difference between them.

The obtained data was uzed when constructing the electric equivalent circuit (EEC) for different ranges of the degree of implementation X. It is revealed that the optimal coincidence between the experimental data and the simulation results is observed with the application of the scheme illustrated in Fig. 7, which is structurally close to that proposed by the authors of [7].
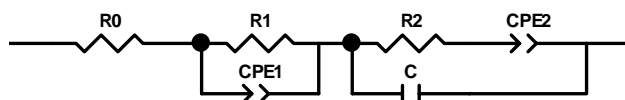

Fig. 7 – Electric equivalent circuit (EEC) used for fitting of the Nyquist curves obtained for the LPS with the cathodes based on mesoporous γ-Fe$_2$O$_3$

The circuit contains the series-connected resistance R_0, link R_1-CPE$_1$ and link R_2-CPE$_2$-C. In this circuit, R_0 corresponds to the electrolyte resistance and, to a small degree, to the lead contacts. R_0 varies little during the discharge in the range of 5-10 Ohm. The constant phase elements CPE were used to provide the flexibility of impedance modulation. It is possible to stay that link CPE simulates the diffusion process of Li$^+$ ions in the cathode material after its accumulation on the particles surface. Deviation of the CPE$_1$P values from 0.5 is explained by the complexity of the cathode material surface morphology, namely, by its fractal properties. In this case, the Fick law is not fulfilled, diffusion cannot be considered linear and semi-infinite, and classical Warburg element is inapplicable. The value of CPE$_1$P varies little up to the values of $x \approx 0.5$. Link R_1-CPE$_1$ reflects the course of a single-stage electrochemical reaction on the electrode/electrolyte interface. In turn, link R_2-CPE$_2$-C describes accumulation of Li$^+$ ions on the surface of the cathode material and its diffusion on this surface. In this case, element C means the adsorption capacity, CPE$_2$ characterizes the percolation diffusion of Li$^+$ ions, element R_2 characterizes the charge transfer process.

4. CONCLUSIONS

The mesoporous γ-Fe$_2$O$_3$ synthesized by citrate sol-gel method as the cathode material in LPS was tested, and the electrochemical processes occurring at the discharge were traced. Based on the results of chronopotentiometry and description of the discharge process by the Frumkin adsorption isotherm, we proposed the operating model of LPS with the cathode on basis of mesoporous γ-Fe$_2$O$_3$, which provides for the accumulation of Li$^+$ ions on the surface of the cathode material/electrolyte interface at the discharge and penetration of Li$^+$ ions into the channels of the material crystal structure.

By the impedance spectroscopy method it is established that diffusion of Li$^+$ ions over the surface positions and deep into the material crystal lattice is observed in the discharge of LPS with the cathode based on mesoporous γ-Fe$_2$O$_3$ during the whole process. Filling of the crystal structure channels for the value of the degree of implementation of $x \leq 0.4$ leads to a sharp reduction of the volume diffusion coefficient in the range of 10^{-10}-10^{-13} cm^2/s. At the same time, the percolation diffusion coefficient of Li$^+$ ions over the surface also decreases (10^{-10}-10^{-12} cm^2/s). The subsequent discharge of LPS is accompanied by a monotonic decrease in the diffusion coefficients.

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