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Phase transitions and guest positions state in the nanodisperse TiO₂ caused by laser irradiation

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The laser irradiation effect on the guest positions state in TiO₂ (anatase) that facilitates lithium ions access to these positions was studied. The method of chemical potential spectroscopy revealed sharp voltage drops and the associated minima in the dependence of the intercalation degree x on the electromotive force $\varepsilon dx/d\varepsilon$, caused by host-guest system ordering and by coexistence of two phases. From the analysis of the entropy change ΔS in dependence on the introduced lithium amount, it was found that ΔS increase is associated with additional guest positions generation and an increase of the oscillational degrees of freedom quantity in the intercalant. The combined effect of laser irradiation and iron doping on nanodispersed TiO₂ provides a stable discharge voltage over a wide range of lithium guest load.

Keywords: anatase, laser irradiation, intercalation, Mössbauer spectroscopy.

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Introduction

The search for crystalline solids suitable for intercalation is one of the urgent problems of materials science, which determines new research directions and expected progress in this field of knowledge. In the fundamental aspect, it is necessary to establish the requirements for the properties of a solid that will allow it to be used as a "host" matrix for intercalation. As a result of theoretical and experimental studies, it was found that intercalation is possible for bodies with a highly anisotropic bond character, capable of donor-acceptor charge exchange with the introduced "guest" components. In addition, these structures must be chemically and thermodynamically stable during intercalation, must ensure topotacticity of the process, and must have structural affinity for the "guest" particles symmetry. However, subsequent studies showed that the above formulation limits not only the class of possible "host" role candidates, but also narrows the diversity of the physical interactions that can lead to intercalation. In fact,

experimental data indicate the ability to intercalate all crystalline solids that possess or are capable of forming "guest" positions (degrees of freedom) in them, and the entire known spectrum of interactions (from Coulomb to dispersion) can be the driving force for that. However, this does not mean that a certain "guest" component can directly intercalate any matrix and vice versa, the latter does not necessarily serve as a "host" for any intercalating component, since the possibility of forming a particular intercalation compound (a specific "host-guest" system type) is determined by certain thermodynamic and kinetic regularities.

Nanomaterials combined with intercalation process (as a generation mechanism for the current-forming reactions in lithium power sources) made it possible to use a fairly wide class of compounds obtained using nanotechnology as cathode materials [1]. This includes titanium dioxide, the structure and physicochemical properties of which are in the focus of a significant amount of experimental and theoretical research. Such interest is due to the possibility of obtaining various modified forms

of titanium dioxides, including nano-dispersed and nanocomposite, which are unique "host" materials for intercalation nanotechnologies. In addition, titanium dioxide has a number of practical advantages: it is readily available, chemically stable, inexpensive and non-toxic.

In recent years, lithium intercalation into rutile and anatase TiO₂ structures has been intensively studied. It was shown that in Li_xTiO₂ the maximum electrochemical introduction varies within the range of $0 < x < 1$ for rutile and $0.5 < x < 1$ for anatase [2]. The authors explain the difference between intercalation limits in these works by the temperature effect. It is assumed that diffusion can be a limiting factor for the rutile and anatase characteristics and for the different materials' characteristics too, like CoO₂ and MnO₂. Studies of the Li_xTiO₂ intercalate are mainly focused on "guest" positions identification and their places in the "host" material [3]. However, individual studies do not provide an intercalation processes complete picture in titanium dioxides, which prevents their maximum effective use as electrical energy source materials.

I. Experimental, discussion of the results

The intercalation degree is also determined by the guest positions (that can be filled with the lithium ions) presence in the "host" material as it is mentioned in the introduction. One of the possible ways to alter their quantity is laser modification (irradiation) of the material. Nanodispersed titanium dioxide with a free surface of 73 m²/g (synthesized by titanium tetrachloride pyrogenic hydrolysis in a hydrogen-air torch at 1370 K temperature with TiO₂ outcome as anatase and rutile mixture), was chosen as the research object due to the purpose of experimental substantiation of this hypothesis. The average particle size in the obtained TiO₂ was $10 \div 60$ nm [4].

X-ray analysis (Fig. 1) exhibits anatase and rutile structure ratio as 71 % to 29 %:

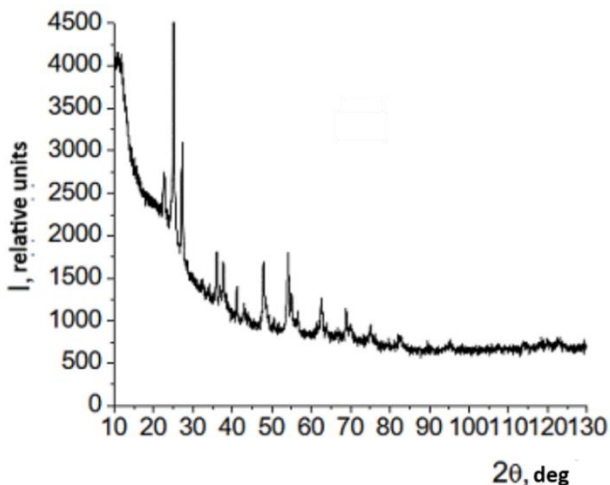


Fig. 1. X-ray diffraction pattern of the initial nanodispersed TiO₂ (Cu anode).

The initial titanium dioxide samples were irradiated with pulses from a laser operating in a Q-switched mode-

locking regime (pulse duration $\tau = 15$ ns, pulse energy $E = 0.015 - 0.02$ J/cm², pulse repetition rate $f = 40$ Hz, irradiation duration 5 minutes).

It is known that one of the methods that provides significant increase of guest positions number along with facilitated access of lithium ions to them, is to disperse cathode material. At the same time, if particle sizes would be less than some threshold value, cathode could undergo significant chemical and physical properties' changes.

Using the chemical potential spectroscopy method for the systems studied (Fig. 2), it can be asserted that the sharp voltage drops and the associated minima on $dx/d\varepsilon$ are caused by the this system ordering, and the horizontal sections on the ε - x are associated with by them, infinite discontinuities in the regions $1.3 < x < 2.2$ and $0.6 < x < 1$ (respective intervals for the initial and laser-irradiated TiO₂), probably correspond with a first kind phase transition caused by a strong "guest-host" interaction with the long-range order formation. The latter means that two phases coexist in these concentration areas of the "guest" load. It is confirmed by the curves (Fig. 2) that exhibit infinite discontinuities.

As a result of laser irradiation, the specified concentration interval shifts to the left along the guest load axis and narrows to $\Delta x = 0.4$. A similar picture is observed when the temperature increases to 320.5 K, at which infinite discontinuities are observed in the regions $1.1 < x < 1.7$ and $0.35 < x < 0.65$. For this TiO₂, in the vicinity of $x = 0.5$ and 3.5 and $x = 1.85$ and 3.065 , jumps in the dependence are observed on the indicated curves $\frac{\partial x}{\partial \varepsilon} = f(x)$ (Fig. 2), which are associated with second kind phase transitions.

It is shown on the graphs for the ΔS entropy change dependence on the introduced lithium amount (Fig. 3 and Fig. 5) and temperature (Fig. 4 and Fig. 6) within the interval $0 < x < 1.5$ for the initial TiO₂ and within the interval $0 < x < 1.2$ for the laser irradiated, that ΔS is negative in the indicated interval.

In addition, a steep ΔS observable change characterises the first kind phase transition. The growth of the "guest" load leads to ΔS value increase, presumably due to the beforementioned effect of generating additional guest positions and a quantity increase of oscillating degrees of freedom for the intercalant (positive values) in the interval $1.5 < x < 4$ (Fig. 3 and Fig. 5).

A mass spectrometric study of the structure of the TiO₂ "host" material with different degrees of lithium incorporation ($0 < x < 4.0$) was conducted. It was established that the distribution of Li along the thickness of the near-surface layer has the form shown schematically in Fig. 7. The maximum intensity of the Li ion mass line at the initial moment of etching (section I in Fig. 7) is most likely caused by the effect on the sputtering coefficient and the charge state of the sputtered components of the oxide state of the surface and uncontrolled impurities adsorbed here. Within the margin of error for all the tested samples, this region has approximately the same thickness within 20 - 30 nm. At the same depths, the intensity of the mass peaks of Na, Ca, and N adsorbed on the surface drops to a minimum value (almost to the background level).

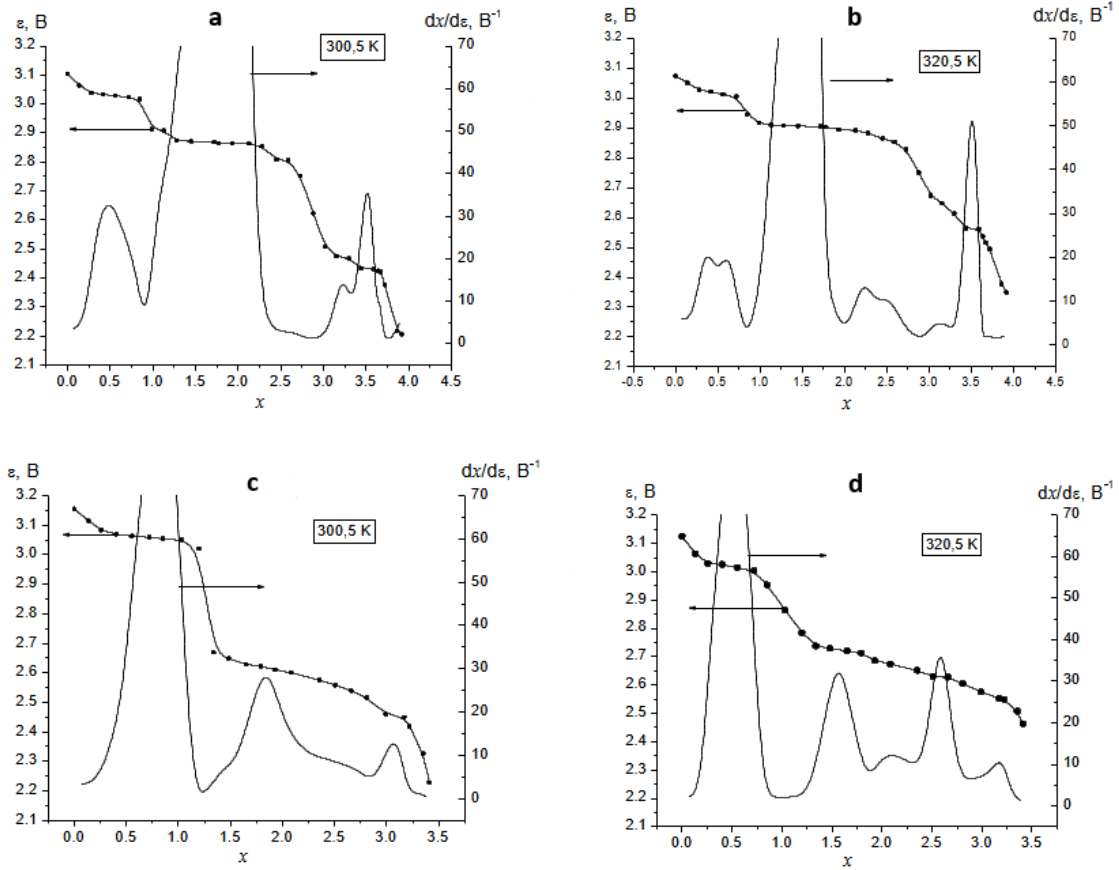


Fig. 2. Dependence of electrochemical cells' electromotive force and differential capacity on the introduced lithium concentration at different temperatures, prepared on the basis of initial TiO₂ (a, b) and laser irradiated TiO₂ (c, d).

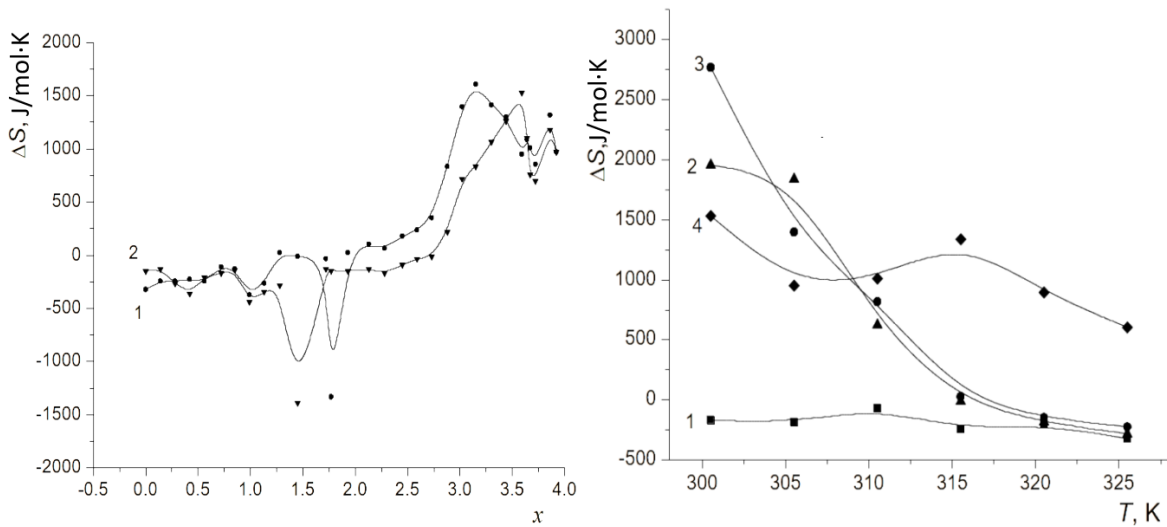


Fig. 3. Dependence of the lithium dissolution entropy change in the initial TiO₂ on its concentration at 300 K (curve 1) and 320 K (curve 2).

Fig. 4. Temperature dependence of the lithium dissolution entropy change in the original TiO₂ for different concentrations of lithium ions: 1 - $x = 0.56$; 2 - $x = 1.72$; 3 - $x = 2.13$ and 4 - $x = 3.59$.

Again, at the same depths, the Ti line intensity grows from a minimum value to reach saturation near the surface and remains practically unchanged there. With the exception of a thin transition layer, intercalated lithium is spatially homogeneously distributed in the volume of TiO₂ itself.

The results of lithium cells operational parameters'

studies (specific capacitance C_s and specific energy E_s), with the studied materials as a cathode, are shown in table 1.

Thus, in the process of TiO₂ electrochemical intercalation by lithium ions, heterophase states are formed there in the corresponding concentration intervals. An increase of the processing temperature leads to the

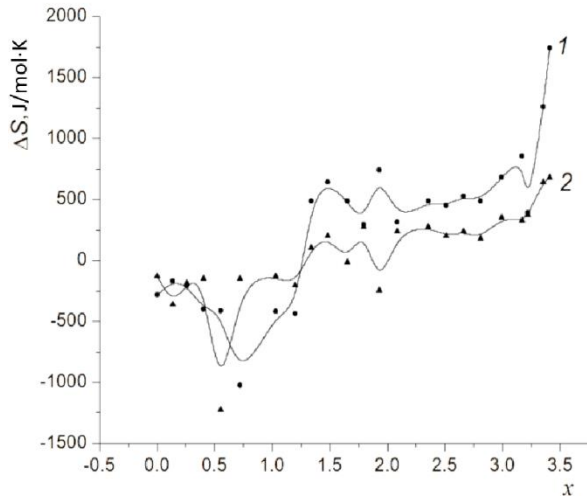


Fig. 5. Dependence of the lithium dissolution entropy change in laser irradiated TiO₂ on its concentration at 300 K (curve 1) and 320 K (curve 2).

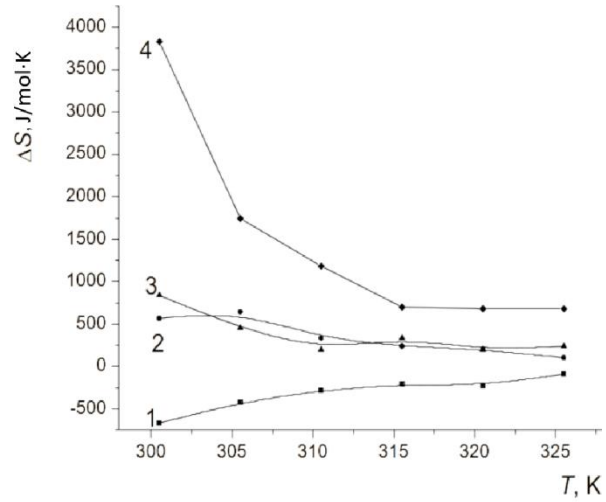


Fig. 6. Temperature dependence of the lithium dissolution entropy change in laser-irradiated TiO₂ for different concentrations of lithium ions: 1 - $x = 0,55$; 2 - $x = 1,481$; 3 - $x = 2,51$ and 4 - $x = 3,41$.

indicated intervals narrowing. A similar effect is achieved with pulsed laser irradiation of the initial TiO₂. In addition, laser irradiation of the material leads to this electrochemical cell discharge voltage slight increase but reduces the incorporated lithium amount.

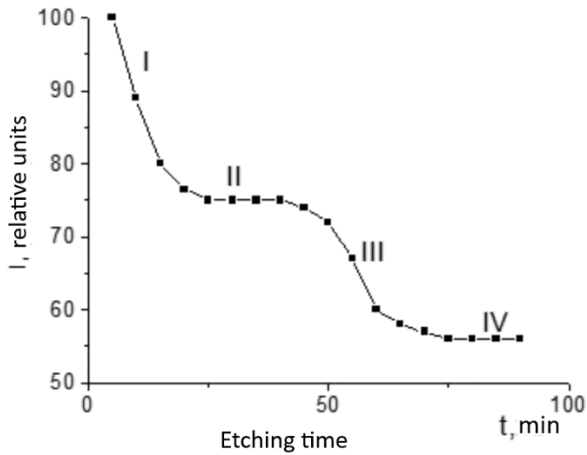


Fig. 7. Dependence of the intensity of the Li mass line intercalated in the TiO₂ "guest" structure (1370 K) on the ion etching time.

Table 1.

Discharge characteristics of electrochemical cells made on the basis of original and laser irradiated nanodisperse TiO₂

Sample	x	C_s , A·h/kg	E_s , W·h/kg
TiO ₂ initial	3.95	1320	2700
TiO ₂ laser irradiated	3.41	1140	2490

At the low degrees of electrochemical intercalation $x = 0 \div 1.5$, all lithium is homogeneously distributed within the intercalate volume. An increase in the intercalation degree of up to $x = 1.6 \div 4.5$ along with high

cathodic polarization current densities leads to the entry of lithium ions into the volume of TiO₂ and causes the formation of a lithium concentration gradient in the direction of the electric field. This process blocks both further intercalation and passive surface layer (formed by lithium ions) growth.

The combined effect of laser irradiation and Fe doping on the electrochemical properties of nanodispersed TiO₂ was studied.

Nanodispersed rutile form TiO₂ with 270 nm average particle size was used as the starting material, which was thermally modified by solid-phase sintering with nanodispersed α -Fe and magnetite Fe₃O₄ at a temperature of 620 - 670 K in a vacuum with a content of 10 - 20 wt.% modifying substance. The homogenized mixture was applied with a thin layer (at the rate of 3 mg/cm²) on a nickel mesh, after which it was sintered in a vacuum at a temperature of 670 K for 1 hour. The samples were irradiated with pulses from a laser operating in the modulated Q mode (pulse duration $\tau = 15$ ns, pulse energy $E = 0.015 - 0.02$ J/cm², pulse tracking frequency $f = 56$ Hz, irradiation duration $t = 1 - 5$ min). X-ray images of the original, thermally modified, and laser irradiated samples are shown in Fig. 8.

The X-ray phase analysis of all systems exhibits stability of the TiO₂ rutile form during the process of thermal and laser modification. The change in the parameters of the tetragonal syngony lattice is given in the table 2.

Comparative curves of the concentration dependence of the maximum degree of Li⁺ intercalation are shown in Fig. 9.

It was established that the laser annealing of TiO₂ (rutile) initial powders also leads to a maximum guest load decrease. This effect is most likely caused by laser compensation of structural defects. The situation changes with laser irradiation of titanium dioxide previously modified with α -Fe and Fe₃O₄. Thus, if for non-irradiated samples the α -Fe concentration growth leads to a decrease in x_{max} , and the Fe₃O₄ concentration growth leads to an

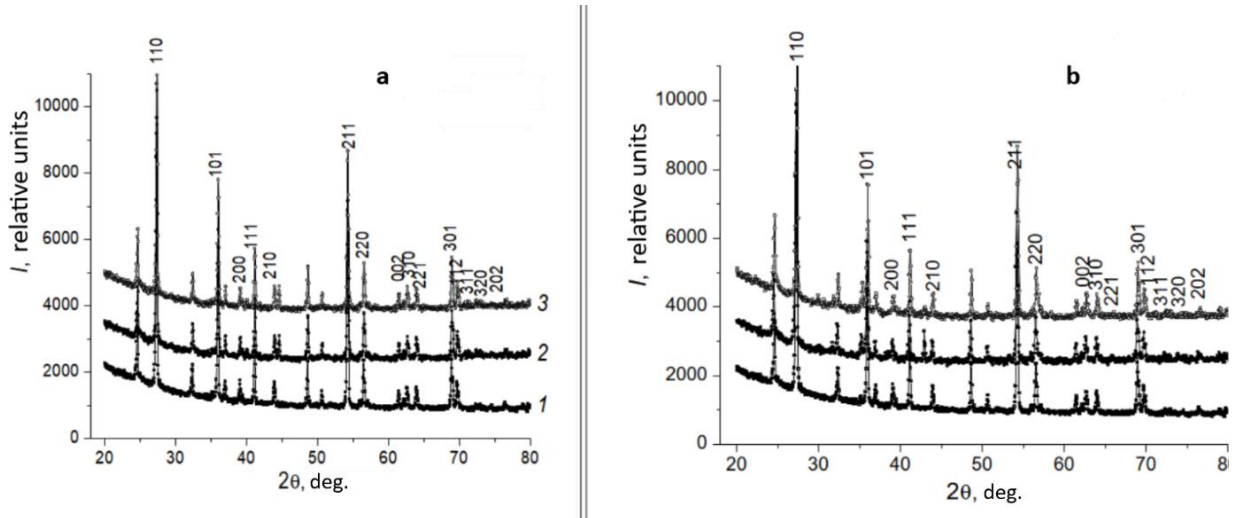


Fig. 8. Comparative X-ray images of initial, thermally modified and laser-irradiated cathode materials:
 a: 1 – TiO₂; 2 – (TiO₂)_{0,88}·(α-Fe)_{0,1}; 3 – (TiO₂)_{0,88}·(α-Fe)_{0,1} – laser irradiated.
 b: 1 – TiO₂; 2 – (TiO₂)_{0,77}·(Fe₃O₄)_{0,2}; 3 – (TiO₂)_{0,77}·(Fe₃O₄)_{0,2} – laser irradiated.

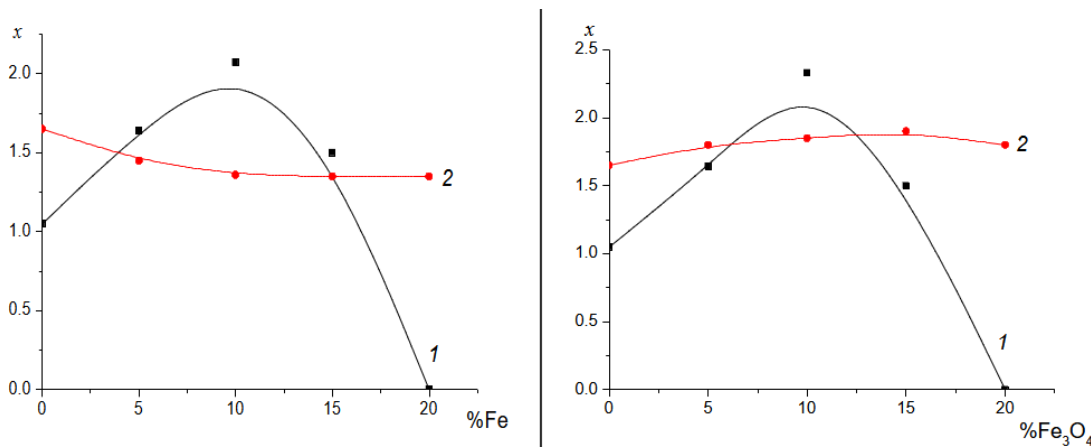


Fig. 9. Comparative curves of the concentration dependence of the maximum degree of Li⁺ intercalation of the original (1) and laser-irradiated TiO₂ (2) on the content of α-Fe and Fe₃O₄ in the cathode.

increase in x_{max} , then the concentration curves of laser-irradiated samples lose their monotonous pattern, and a maximum is observed for the 10 % concentration α-Fe and Fe₃O₄. The discharge parameters of the studied systems are given in the table 3.

The X-ray images (Fig. 8) analysis finds only diffraction reflexes for TiO₂ (rutile), α-Fe (a) and Fe₃O₄ (b), indicating that magnetite can participate in intercalation processes since it has spinel structure with a sufficient number of guest positions. As a result of pulsed laser annealing of TiO₂ + Fe₃O₄ samples, guest positions number increases due to a slight change in their introduction energy. It can be assumed that similar irradiation of samples doped with α-Fe leads to the α-iron phase oxidation and a new phase formation that is capable of Li⁺ intercalation. The region of discharge voltage stability moves towards higher values of x , while the discharge voltage nominal value increases by approximately 0.1 V. On X-ray images, the laser irradiation effect of such samples is manifested in the low intensity lines appearance from the phase, which could not be identified due to insufficient method sensitivity. Fig. 10 shows Mössbauer spectra of Fe⁵⁷ from modified and laser irradiated samples with a 10 % dopant content.

Table 2. Structural parameters of nanocrystalline titanium dioxide at 293 K

Sample	Lattice parameters, nm			
	Initial		Laser irradiated	
	a	c	a	c
TiO ₂	0.4589	0.2955	0.4587	0.2954
TiO ₂ +20%Fe	0.4590	0.2956	0.4590	0.2956
TiO ₂ +20%Fe ₃ O ₄	0.4582	0.2951	0.4584	0.2953

Table 3. Discharge characteristics of electrochemical cells made on the basis of original and laser irradiated nanodisperse TiO₂

	Cathode material	x	C_s , A·h·kg ⁻¹	E_s , W·h·kg ⁻¹
Initial	TiO ₂ +a-Fe	1.36	459	951
	TiO ₂ +Fe ₃ O ₄	1.93	594	1301
Laser irradiated	TiO ₂ +a-Fe	2.07	480	1096
	TiO ₂ +Fe ₃ O ₄	2.73	686	1550

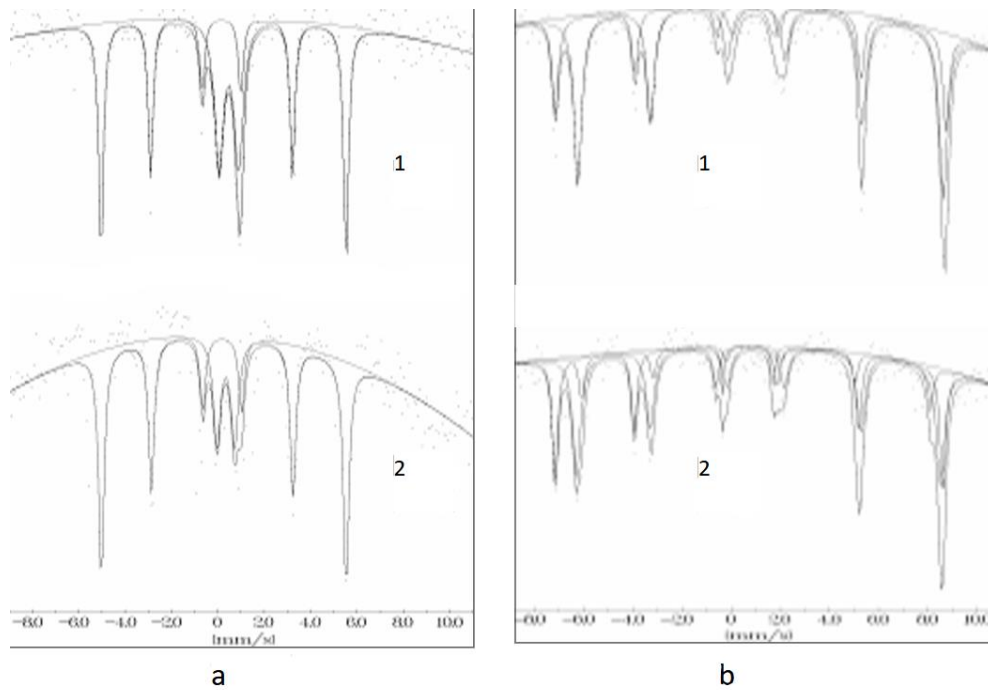


Fig. 10. Mössbauer spectra of iron (a) and magnetite (b) modified samples before (1) and after (2) laser annealing. Alloying additive content 10%.

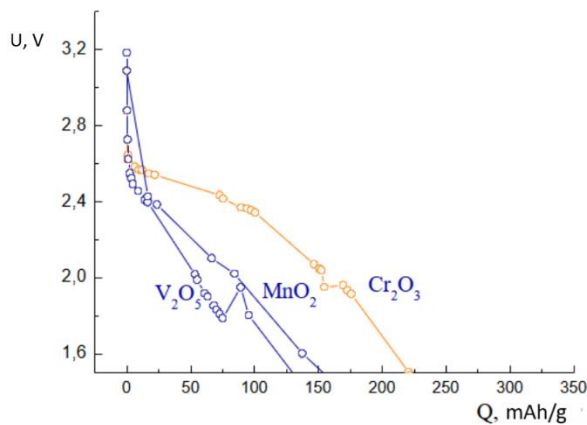


Fig. 11. Effect of 3d elements (≤ 1 wt.%) oxides on the TiO₂ discharge capacity during its lithium co-intercalation

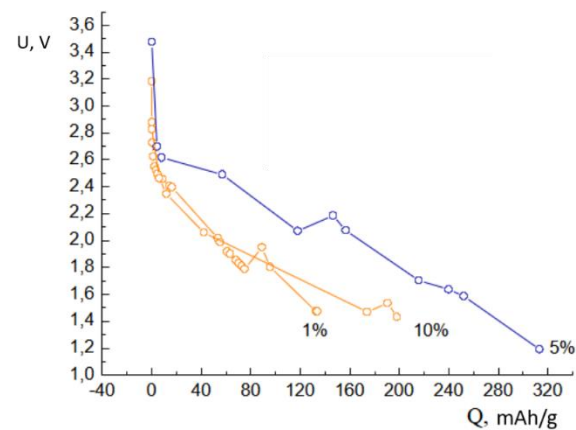


Fig. 12. 3d elements oxides' concentration influence on the silicon discharge capacity during its lithium co-intercalation.

The spectra were processed with Mössbauer application "MossWin". α -Fe-doped samples exhibit the presence of Fe³⁺ ions significant amount (~36 % of the total iron content) in the paramagnetic state (Fig. 10,a), which is evidenced by the presence of an intense paramagnetic doublet in the spectrum.

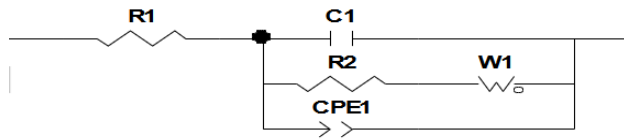
From the point of view of intercalation-cathode characteristics, it is most appropriate to use TiO₂ samples modified with 10 % Fe₃O₄ and laser annealed. Such materials ensure a stable discharge voltage in a wide range of lithium "guest" load. Mössbauer's studies show that the paramagnetic Fe²⁺ doublet formed during the sintering of Fe₃O₄ with TiO₂ (quadrupole splitting of the subspectrum $\Delta Q = 1.58$ mm/s, integral intensity 7.2 %) ferritizes upon laser irradiation, its intensity decreases to ~4 % due to the additional appearance of sextuplet with ~13 % of integral intensity and a high quadrupole splitting value (commensurate with the rest of the sextuplets), that

corresponds to Fe³⁺ in a state with magnetically split levels. This non-equivalent position is also not detected by X-ray diffraction as a separate phase but exists due to the surface saturation of the TiO₂ structure with iron [5].

A similar situation occurs when the "host" material is TiO₂, but only at low (≤ 1 wt.%) concentrations of 3d-elements oxides (Fig. 11). As their concentration increases, the Gibbs molar energy change value of lithium co-intercalation has a non-monotonic character (Fig. 12).

For a 5 % Fe₃O₄ content, the intercalation process kinetic dependencies are presented in the form $-\text{Im}Z = f(\text{Re}Z)$ can be conditionally divided into three groups, respectively, for values $0 < x \leq 0.72$, $x \sim 1$ and $1 < x \leq 1.36$. The Randles-Ershler scheme modified by the constant phase element (CPE) can be compared to the first of the specified groups (Fig. 13-14).

For the second group, it is supplemented with a block that reflects the processes in the passivation film on the



<u>Element</u>	<u>Freedom</u>	<u>Value</u>	<u>Error</u>	<u>Error %</u>
R1	Fixed(X)	256,4	N/A	N/A
C1	Fixed(X)	1,8173E-6	N/A	N/A
R2	Fixed(X)	609,4	N/A	N/A
W1-R	Fixed(X)	435,6	N/A	N/A
W1-T	Fixed(X)	1	N/A	N/A
W1-P	Fixed(X)	0,48879	N/A	N/A
CPE1-T	Fixed(X)	6E-5	N/A	N/A
CPE1-P	Fixed(X)	0,43676	N/A	N/A

Chi-Squared: 0,0095308
 Weighted Sum of Squares: 0,29545

Data File: D:\173x024m.POO
 Circuit Model File: D:\TiO0.24fin.mdl
 Mode: Run Fitting / Freq. Range (0,01 - 100000)
 Maximum Iterations: 100
 Optimization Iterations: 0
 Type of Fitting: Complex
 Type of Weighting: Calc-Modulus

Fig. 13. Equivalent scheme for simulating Li 0.24 TiO₂ <5% Fe₃O₄> co-intercalation processes.

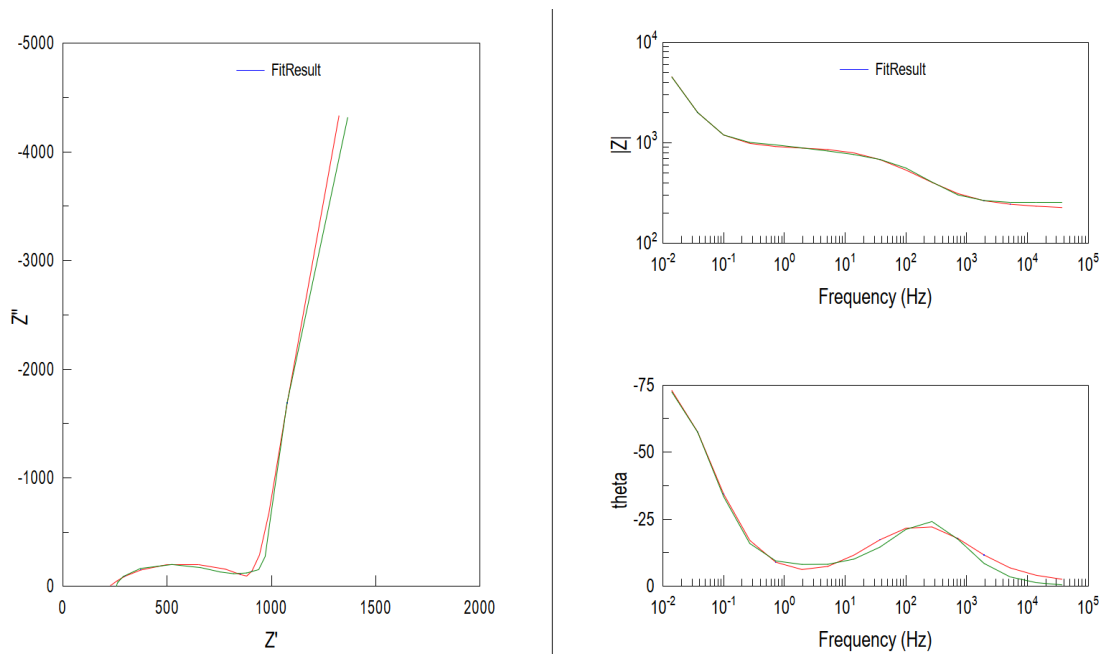


Fig. 14. Experimental and theoretical ($R_1=256.4$ Ohms; $R = 609.4$ Ohms; $C_1 = 1.82 \cdot 10^{-6}$ F; $W = 35.6$ Ohms; $CPE = 0.4367$) impedance characteristics of the co-intercalation process of Li 0.24 TiO₂ <5% Fe₃O₄>.

electrode surface. The third group of Nyquist diagrams indicates diffusion control strong growth, which must be supplemented by the depleted layer capacity inclusion into the intercalate volume.

Conclusions

1. The maximum degree of lithium-cation

intercalation depends mainly on the particle size and production method of the cathode material. Its highest value with a small Gibbs energy $\Delta G(x)$ change is reached when using nanodispersed anatase and rutile TiO₂ in the ratio of 81 % to 19 % with 8 nm average particle size due to the positive value of the $\Delta S(x)$ lithium dissolution entropy. This positive entropy value is associated with a significant contribution of oscillational degrees of freedom of the "guest" Li⁺ ions in the studied structure.

2. Pulsed laser irradiation of nanodispersed TiO₂ causes concentration intervals narrowing of heterophase states due to the structural defects laser compensation effect. It naturally leads to a certain drop in the "guest" loading degree when the discharge voltage increases.

3. It was found that laser irradiation and long-term thermal processing on nanodispersed rutile TiO₂ lead to a change in lattice constants without altering their type. At the same time, nanocomposites TiO₂<Fe> and TiO₂<Fe₃O₄> laser irradiation stimulates intercalation processes in electrochemical systems based on them, stabilizes and increases the discharge voltage and leads to a higher "guest" load value.

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- [1] B.K. Ostafiychuk, I.M. Budzuliak, I.I. Hryhorchak, I.F. Myroniuk. Nanomaterials in the electrical energy generation and storage devices. (Ivano-Frankivsk, 2007); ISBN 978-966-640-216-8.
- [2] M.V. Koudriachova, N.M. Harrison, S.W. Leeuw. *Effect of Diffusion on Lithium Intercalation in Titanium Dioxide*, Phys. Rev. Lett., 86, 1275 (2001); <https://doi.org/10.1103/PhysRevLett.86.1275>.
- [3] B.K. Ostafiychuk, I.M. Budzuliak, I.M. Hasiuk, R.V. Ilnytskyi. *Kβ_{2,5} X-ray Ti emission lines in the nanocrystalline titanium dioxide, intercalated by lithium ions*, Physics and Chemistry of Solid State, 5(2), 271 (2004).
- [4] B.K. Ostafiychuk, I.M. Budzuliak, R.V. Ilnytskyi et al. *Laser irradiation influence on the processes of lithium electrochemical intercalation into the nanodispersed titanium dioxide*. Mat. IV Int. Conf. Neet-2005 [“New electrical and electronic technologies and their industrial implementation”], (Zakopane, Poland, June, 21-24, 2005).
- [5] B. Ostafiychuk, V. Moklyak, V. Fedoriv, A. Hrubciak, Y. Yavorskyi, & S. Yuryev, *Low-temperature Mossbauer studies of the phase composition and structural stability of iron (III) oxide/hydroxide nanocomposite*, Physics and Chemistry of Solid State, 22(2), 307-312 (2021); <https://doi.org/10.15330/pcss.22.2.307-312>.

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Фазові переходи та стан гостьових позицій в нанодисперсному TiO₂, зумовлені лазерним опроміненням

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Досліджено вплив лазерного опромінення на стан гостьових позицій в TiO₂ (анатаз), що полегшує доступ до них йонів літію. Методом спектроскопії хімічного потенціалу виявлені різкі спади напруги та пов'язані з ними мінімуми на залежності ступеня впровадження x від електрорушійної сили $\epsilon dx/d\epsilon$, які обумовлені впорядкуванням в системі господар-гість та співіснуванням двох фаз. З аналізу зміни ентропії ΔS від величини впровадженого літію встановлено, що збільшення ΔS пов'язано з генеруванням додаткових гостьових позицій та зростанням кількості коливних ступеней вільності інтеркаланта. Сумісний вплив лазерного опромінення та легування залізом на нанодисперсний TiO₂ забезпечує стабільну розрядну напругу в широкому інтервалі літійового гостьового навантаження.

Ключові слова: анатаз, лазерне опромінення, інтеркаляція, мессбауерівська спектроскопія.