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Structure of titanium dioxide, doped with Zr and Nb

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Analysis of the structure and phase change of nanodispersed titanium dioxide (obtained using sol-gel method) intercalated with zirconium and niobium (based on the following precursors: zirconium butoxide $Zr(OC(CH_3)_3)_4$ and niobium ethoxide $Nb(OCH_2CH_3)_5$) has been performed. X-ray analysis revealed anatase and brookite phases for TiO_2<Zr> and their transformation into rutile upon annealing at a temperature of 1120 K. It is shown that intercalation of niobium in TiO_2 stabilizes anatase phase (without transformation into rutile).

Keywords: titanium dioxide, zirconium, niobium, intercalation.

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Introduction

The low potential of titanium dioxide relative to metallic lithium, the presence of appropriate guest positions, cheapness and environmental safety give grounds to consider it a promising cathode material in lithium current sources after appropriate modifications. Although the intercalation properties of titanates have already been sufficiently studied using various experimental and theoretical methods, the connection between the crystal structure and the mechanisms of intercalational current generation has not been practically established. The first principles and conceptual foundations of the construction of intercalates indicate that the distribution of electrons in the crystal lattice is also an important factor responsible for intercalation processes. It should be taken into account that in a nanodispersed material the energy spectrum of electrons is significantly different from the spectrum in a massive single crystal and depends on the size of the nanoparticles. With the development of modern technologies, nanosized titanium dioxide as a cathode material is of considerable scientific interest, since the specific area and, accordingly, the number of introduced lithium ions increase. Thus, to improve TiO_2 as a cathode material it is necessary to establish the conditions and modes of its modification under which the introduction of lithium ions is most effective in terms of the functioning of lithium current sources (LCS). One of the possible modifications is doping the starting material with transition group metals that locally deform the lattice, forming additional channels and expanding the specific surface area to increase the material's intercalation level [1].

Establishing optimal conditions for the synthesis and doping of nanosized titanium dioxide requires studying the structure, physical and electrochemical properties using various modern techniques. It is thanks to them there is possibility to establish the determining factors of the LCS specific capacitance and power.

I. Experimental, discussion of the results

Obtaining nanodispersed titanium dioxide of various forms and modifications is quite relevant today, since nanosized TiO_2, with its significant specific surface area and a structure capable of intercalation is a rather promising material for lithium current sources.

We have obtained a nanodispersed titanium dioxide intercalated with zirconium and niobium that has 20% of addition content by molar mass. Nanocrystalline titanium dioxide intercalated with these elements has a number of advantages: better thermal stability, larger surface area,

and, accordingly, smaller particle sizes. The intercalation of titanium dioxide with zirconium and niobium was carried out according to the scheme presented in Fig. 1, with the addition of a "guest" precursor to titanium isopropoxide. Zirconium butoxide $Zr(OC(CH_3)_3)_4$ has been used for the zirconium intercalation into TiO_2, and niobium ethoxide $Nb(OCH_2CH_3)_5$ for niobium intercalation into titanium isopropoxide accordingly.

The obtained materials were subjected to annealing at temperatures of 670 and 1120 K in air for one hour. The use of annealing is a part of the method of modifying titanium dioxide after its intercalation (since heating affects the physical and electrochemical properties of nanodispersed materials both through coalescence of particles and through dehydration of the structure). At 673 K, the crystal structure does not change, only its dehydration is possible. And accordingly, for the pure titanium dioxide recrystallization of anatase into rutile is observed at 1123 K.

As a result of the syntheses, a series of nanodispersed samples were obtained: undoped titanium dioxide (TiO_2); titanium dioxide intercalated with zirconium (TiO_2<Zr>); TiO_2 annealed and intercalated with zirconium at temperatures of 670 K (TiO_2<Zr>(670 K)) and 1120 K (TiO_2<Zr>(1120 K)); titanium dioxide intercalated with niobium (TiO_2<Nb>); titanium dioxide doped with niobium and annealed at 670 K – TiO_2<Nb>(670 K) and 1120 K – TiO_2<Nb>(1120 K), respectively.

Thus, it is possible to investigate the influence of zirconium and niobium elements on the TiO_2 physical and electrochemical properties using a number of syntheses (carried out using sol-gel technology) to obtain nanosized undoped TiO_2 and TiO_2 intercalated with niobium or zirconium.

X-ray studies of titanium dioxide samples intercalated with zirconium and annealed at 670 and 1120 K made it possible to establish the heating effect on the rate of phases' recrystallization in TiO_2. Titanium dioxide intercalated with zirconium and annealed at 670 and 1120 K is characterized by the anatase phase (Fig. 2, 1-3), the content of which is predominant for all the obtained materials.

Annealing TiO_2<Zr> at 670 K changes the crystal structure of intercalated titanium dioxide compared to both doped / undoped. The narrowing of the broadened X-ray diffraction peaks after annealing is due to the

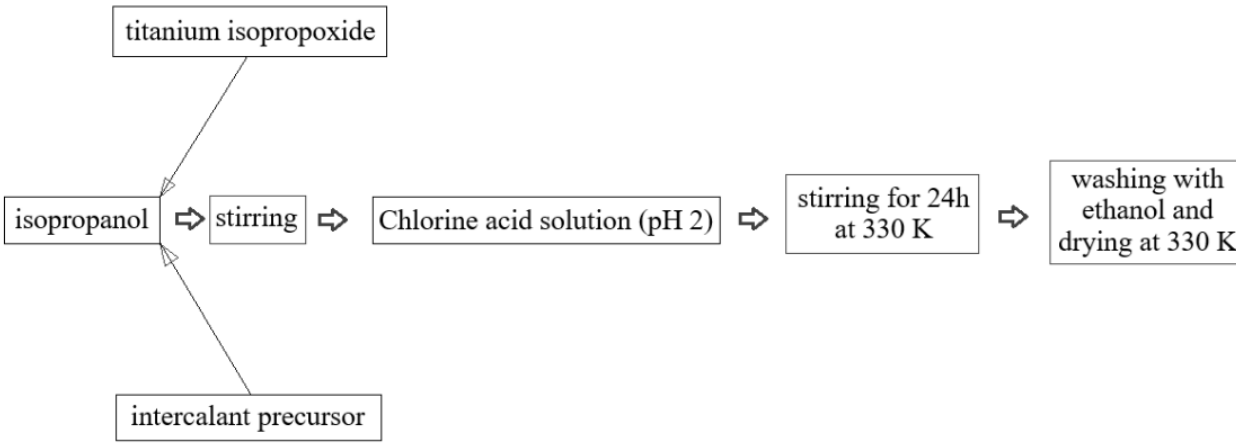

Fig. 1. Sequence diagram for obtaining doped nanodispersed TiO_2 using sol-gel technology.

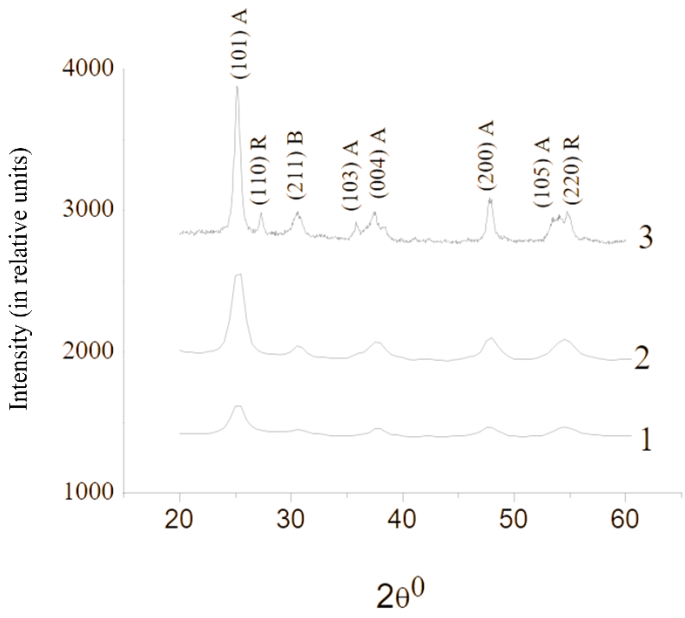

Fig. 2. X-ray diffraction patterns for TiO2 intercalated with zirconium (1) and annealed at 670 K (2) and 1120 K (3).

nanoparticles coalescence. In addition, there is when reflexes do appear ($2\theta = 27.18$; 54..72) that are specific to rutile. After annealing at 1120 K, one could expect a complete transformation of anatase into rutile.

Analysis of X-ray diffraction patterns for the material synthesized by sol-gel technology based on zirconium butoxide showed that this structure corresponds to zirconium dioxide ZrO_2 tetragonal crystal system (space group P42/nmcS) with the values of the crystal lattice constants $a = b = 3.603$ Å, $c = 5.172$ Å (Fig. 3. 5, 2). Annealing at around 670 K (Fig. 3. 5, 2) for one hour causes a significant increase in the size of the coherent scattering region (CSR) and crystallization, since unannealed zirconium oxide is an amorphous material. There are no ZrO_2 reflexes (which are present in Fig. 3) for titanium dioxide intercalated with zirconium, and it suggests that zirconium replaces titanium atoms in the TiO_2 crystal structure.

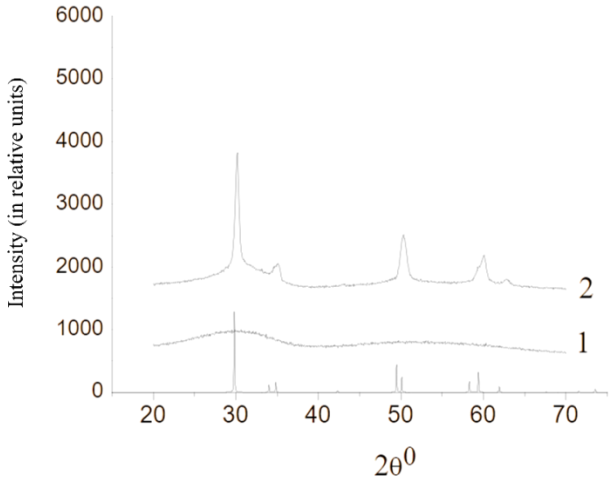

Fig. 3. X-ray diffraction patterns of zirconium dioxide ZrO_2 before (1) and after annealing at 670 K (2).

The percentage content of anatase, rutile and brookite phases and the dimensions of the lattice constants for the original TiO_2 and intercalated with zirconium are presented in Table 1. The effect of zirconium on the crystal structure is reflected by a slight lattice expansion, taking into account the magnitude of the error caused by the substitution of Ti ions by Zr. For example, the crystal lattice constants of anatase for zirconium-intercalated TiO_2 are $a = 3.823$ Å, $c = 9.550$ Å, while for the original TiO_2 they are $a = 3.797$ Å i $c = 9.475$ Å, respectively.

It is worth noting that intercalation with zirconium increases the amount of brookite in the titanium dioxide structure from 4 to 20%, i.e. zirconium ions contribute to the "self-organization" of atoms into the brookite rhombohedral structure. Accordingly, annealing reduces its content due to transformation into anatase, since it is the least stable phase of TiO_2 when heated. With increasing temperature (1120 K) recrystallization of anatase and brookite into rutile occurs, the amount of which in TiO_2<Zr> at 1120 K is ~ 27% and 62% / 11% of anatase / brookite. Thus, zirconium does not contribute to the absolute formation of rutile and stabilizes the brookite phase.

X-ray diffraction analysis of the material obtained by intercalating TiO_2 with niobium and annealed at 670 and 1120 K indicates that its structure differs from TiO_2<Zr> primarily by single-phase content. Only anatase reflexes are recorded on the diffractogram. The peaks of the X-ray diffractograms are broadened, which indicates the nanodispersity of TiO_2<Nb>. The sizes of niobium ions are much smaller than zirconium ions and are commensurate with titanium, although they differ in their charge state – Ti^{+4}, and Nb^{+5}. According to the obtained X-ray diffractograms, the crystal structure of titanium dioxide does not change when TiO_2 is intercalated with niobium [2].

The anatase form of TiO_2 intercalated with niobium is heat-resistant to transformation into rutile according to the diffraction patterns (Fig. 4. 1-3). The temperature at which the crystalline transformation of TiO_2 occurs depends on the concentration of oxygen vacancies. Niobium is an impurities donor and (in addition to increasing conductivity) there is also a decrease in oxygen vacancies (due to its 5+ charge state) even with increasing temperature. The temperature of anatase-rutile transformation grows with increasing amount of this element in TiO_2, although at 1120 K no rutile reflections are detected in X-ray diffraction patterns. The narrowing of diffraction lines after annealing is insignificant. At 1120 K the titanium diniobite phase $TiNb_2O_7$ is formed with the content at the level of (~ 4%) [3].

Table 1.

Crystal lattice parameters for TiO_2, intercalated with Zr

	Lattice constants	TiO_2	TiO_2<Zr>	TiO_2<Zr> 670 K	TiO_2<Zr> 1120 K
Anatase	*a*	3.799±0.009	3.823±0.009	3.800±0.004	3.797±0.0005
	b	3.799±0.009	3.823±0.009	3.800±0.004	3.797±0.0005
	c	9.477±0.027	9.550±0.027	9.540±0.013	9.586±0.002
	Content, %	*96.16*	*80.27*	*87.5*	*62.12*
Brookite	*a*	9.055±0.070	9.261±0.070	9.247±0.039	9.288±0.012
	b	5.472±0.033	5.456±0.033	5.464±0.020	5.487±0.006
	c	5.341±0.032	5.262±0.032	5.186±0.014	5.176±0.004
	Content, %	*3.84*	*19.73*	*12.5*	*10.28*
Rutile	*a*	–	–	–	4.605±0.001
	b	–	–	–	4.605±0.001
	c	–	–	–	2.976±0.001
	Content, %	–	–	–	*27.6*

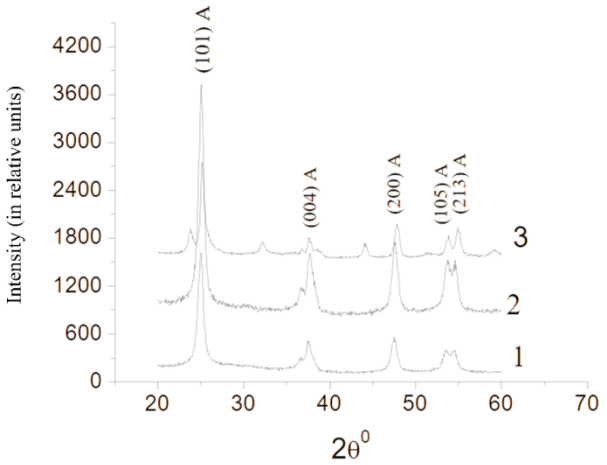

Fig. 4. X-ray diffraction patterns for the initial TiO_2 intercalated with niobium (1) and annealed at 670 (2) and 1120 K (3).

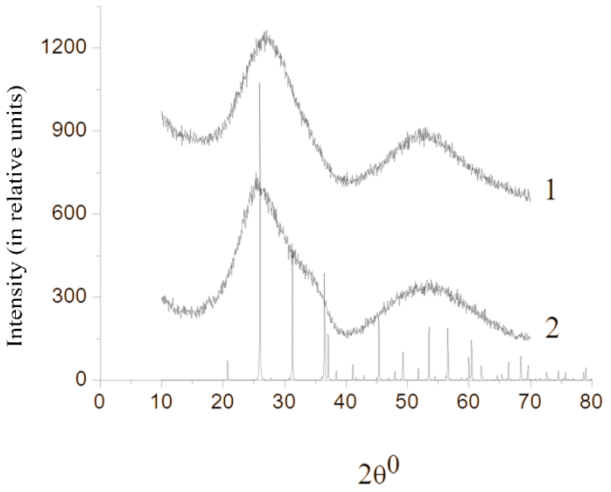

Fig. 5. X-ray diffraction patterns for synthesized niobium oxide before (1) and after annealing at 670 K (2).

Analysis of X-ray diffraction patterns (Fig. 5) obtained for the material synthesized on the basis of the niobium ethoxide precursor (1) and annealed in the temperature range of 670 K (2) allowed us to identify the structure of niobium oxide Nb_2O_5. Unlike zirconium dioxide the temperature effect on the course of the diffraction patterns in this case is insignificant.

Similarly, as in the case of TiO_2 intercalated with zirconium, no reflections that are characteristic of niobium oxide are found in the diffractograms for TiO_2<Nb>. Thus, TiO_2 with niobium (as with zirconium) is capable of forming a solid solution of $Nb_xTi_{1-x}O_2$. At the same time, according to our results, the formation of anatase structure for this solid solution can be possible when niobium content is up to 20%.

Similarly, a quantitative analysis of titanium dioxide is presented regarding the content of its inherent phases and the size of the lattice constants (Table 3. 2). For unannealed TiO_2<Nb>, taking into account the error of determination, a slight increase in the lattice constants is observed. The intercalated material is characterized by the anatase phase and the absence of brookite. After 670 K, the structure is preserved. At 1120 K, a two-phase system is formed: anatase and titanium diniobite without the transformation of anatase into rutile [4].

The average values of the CSR <*d*> for nanopowders, that are determined by the main peaks of X-ray diffractograms using the Scherrer equation, are presented in Tables 3 and 4. From the comparison of the data in both tables, it is seen that the CSR values of zirconium-doped TiO_2 are somewhat smaller than those of TiO_2 doped with niobium. Annealing of the samples at a temperature of 1120 K leads to their growth from 4 to 15 nm that is explained by the coalescence of particles and is reflected in the diffraction peaks width.

Zr intercalation in TiO_2 does not significantly affect the structure and CSR, as well as the spherical shape of the nanoparticles. After annealing at 1120 K, the nanoparticles coalesce and the CSR increases threefold.

Table 2.

Crystal lattice parameters for TiO_2<Nb>

	Lattice constants	TiO_2	TiO_2<Nb>	TiO_2<Nb> 670 K	TiO_2<Nb> 1120 K
Anatase	*a*	3.799±0.008	3.823±0.013	3.816±0.020	3.795±0.009
	b	3.799±0.008	3.823±0.013	3.816±0.020	3.795±0.009
	c	9.477±0.005	9.575±0.006	9.533±0.011	9.531±0.011
	Content, *%*	*96.16*	*100*	*100*	*85.8*
Brookite	*a*	9.055±0.030	–	–	–
	b	5.472±0.021	–	–	–
	c	5.341±0.007	–	–	–
	Content, *%*	*3.84*	–	–	–
Titanium diniobite	*a*	–	–	–	11.871±0.014
	b	–	–	–	3.813±0.009
	c	–	–	–	20.373±0.007
	Content, %	–	–	–	4.2

Table 3.

Sizes of the crystallites in TiO_2<Nb> nanopowders

Material	TiO_2	TiO_2<Nb>	TiO_2<Nb> 670 K	TiO_2<Nb> 1120 K
<d>, nm	4	8.71	7.4	15.4

Table 4.

Sizes of the crystallites in TiO_2<ZrO_2> nanopowders

Material	TiO_2	TiO_2<Zr>	TiO_2<Zr> 670 K	TiO_2<Zr> 1120 K
<d>, nm	4	5	6	14

Conclusions

1. It was established that the main phase of TiO_2 is anatase when intercalation level of niobium and zirconium in TiO_2 is 20%. When annealing TiO_2 intercalated with Zr, rutile is formed, while in the case of Nb and annealing at 1120 K the rutile phase is absent.

2. It was found that:

- Non-intercalated, unannealed titanium dioxide has anatase and brookite phases but when annealing at 1120 K absolute recrystallization into rutile occurs;

- Anatase and brookite phases and their transformation into rutile at 1120 K were detected for TiO_2<Zr>;

- When titanium dioxide is intercalated with niobium, the anatase phase is stabilized (its transformation into rutile does not occur) even at a temperature of 1120 K.

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Структура діоксиду титану, легованого Zr і Nb

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Описано структуру та зміну фаз нанодисперсного діоксиду титану (отриманого за допомогою золь-гель технології), інтеркальованого цирконієм та ніобієм (на основі наступних прекурсорів: бутоксид цирконію $Zr(OC(CH_3)_3)_4$ та етоксид ніобію $Nb(OCH_2CH_3)_5$). Методом Х-променевого аналізу виявлені фази анатазу та брукіту для TiO_2<Zr> та їхня трансформація в рутил при відпалі за температури 1120 К. Показано, що інтеркаляція ніобію в TiO_2 стабілізує анатазну фазу (без перетворення в рутил).

Ключові слова: діоксид титану, цирконій, ніобій, інтеркаляція.