The paper presents structural, surface, thermodynamic and kinetic characteristics of titanium dioxide samples obtained by means of alkaline hydrolysis of TiCl₄ by LiOH solutions and further heat treatment. TiO₂ samples have the anatase structure with crystallite size of 7–10 nm. An increase in the heat treatment temperature from 150 °C to 470 °C leads to a decrease in the specific surface area from 404 to 80 m²/g and the total pore volume from 0.340 to 0.152 cm³/g. The influence of electrolyte composition and surface properties of TiO₂ on its behavior in cells with lithium anode investigated by means of galvanostatic cycling and impedance spectroscopy is discussed.

**Key words:** titanium dioxide, surface properties, electrolyte, solid electrolyte interface, quasi-equilibrium voltage

**INTRODUCTION.** Titanium dioxide TiO₂ is a well-studied electrode material for lithium-ion batteries. Among known TiO₂ structural modifications, titanium dioxide with anatase structure is characterized by high specific capacity and its stability during the long-term cycling.

The process of lithium intercalation-deintercalation in the structure of TiO₂ proceeds in accordance with reaction 1, which corresponds to the theoretical specific capacity of 335 mAh/g (for \(x = 1\))

\[
\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2. \quad (1)
\]

However, the experimentally obtained specific capacity, as a rule, does not exceed 200 mAh/g and corresponds to ~0.6 moles of lithium ions reversibly intercalating into the structure of TiO₂. Higher values of discharge capacity are realized at higher temperatures [1] or for TiO₂ nanoparticles of less than 7 nm [2].

There are also publications in the literature with comparatively higher values of specific capacity obtained by cycling of TiO₂ in cells with lithium anode. Specific capacities of 276 mAh/g at the first cycle and 218 mAh/g upon cycling with a coulombic efficiency of 79 % were obtained by the authors [3] for
electrodes consisting of mesoporous TiO$_2$ spheres / graphene composite.

The influence of particle size, structural and surface characteristics of TiO$_2$ on its specific capacity and stability cycling are studied in detail [4–12]. It has been noted that a decrease in particle size and an increase in the specific surface of TiO$_2$ improve its capacity and cycling properties.

It is known that the discharge of TiO$_2$ with the formation of Li$_1$TiO$_2$ compound is thermodynamically possible [13]. However, experimental specific capacities close to theoretical values are not achieved as a result of kinetic difficulties caused by a decrease of diffusion coefficient of lithium at $x > 0.5$.

The reason of the increase in the diffusion coefficient is the formation of Li$_1$TiO$_2$ that complicates the access of lithium cations to the surface of TiO$_2$ particles. At the voltage value of $\sim 1.75$ V, the discharge proceeds in the conditions of simultaneous presence of two phases, namely TiO$_2$ phase and rhombic Li$_x$TiO$_2$ formed as a result of intercalation of lithium. An increase in the thickness of the Li$_x$TiO$_2$ layer leads to a change in the kinetics of intercalation-deintercalation of lithium, changing the nature of discharge-charge curves that turn into a sloping curve with a relatively small plateau at the voltage of $\sim 1.45$ V.

In accordance with the results given in Ref. [14], the quasi-equilibrium voltage on the discharge curve at the voltage region of $\sim 1.75$ V depends on the size of TiO$_2$ particles, and their increase from 15 nm to 300 nm leads to increasing the quasi-equilibrium voltage from 1.802 V to 1.811 V. The authors explain this effect by the difference in the surface energy of the compounds formed upon discharge. The surface energy of $\beta$-Li$_x$TiO$_2$ phase is larger in comparison with the $\alpha$-Li$_x$TiO$_2$ phase, which leads to a higher value of the quasi-equilibrium voltage. It is also noted that the dependence of the values of quasi-equilibrium voltage on the particle size may arise from capillary effects affecting the chemical potential of crystallites. The particle size reduction contributes to increasing the chemical potential of crystallite and thereby reduces the quasi-equilibrium voltage of TiO$_2$ vs. Li/Li$^+$ [14].

In addition to dimensional effects and structural properties of TiO$_2$, specific and kinetic characteristics of lithium intercalation-deintercalation reaction also depend on the electrolyte composition. This is due to the fact that electrical conductivity and the range of electrochemical stability potentials of electrolyte determine the resistance at the phase boundary and in the porous structure of electrode. The effect of electrolyte composition is manifested especially at low voltage discharge. This is due to processes of electrolyte decomposition and solid electrolyte film formation showing up in this voltage region.

The purpose of this work is to determine the effect of annealing conditions of TiO$_2$ on its physico-chemical parameters, thermodynamic and kinetic characteristics in lithium cells with different electrolyte composition.

**EXPERIMENT AND DISCUSSION OF THE RESULTS.** TiO$_2$ samples were synthesized by means of alkaline hydrolysis of TiCl$_4$ by LiOH solutions. Precipitates obtained were washed with distilled water until pH 7 was reached, dried at 150 °C for 10 h in air, and subjected to further thermal treatment at 350–470 °C with total duration up to 46 h (350 °C – 4 h, 350 °C – 26 h, 350 °C – 40 h, 350 °C – 40 h + 470 °C – 6 h).

The phase composition of the samples was studied by means of X-ray diffraction (XRD) on
a DRON 4-07 diffractometer (LOMO, Russia) with Cu-Kα radiation. The crystallite size was calculated by the Scherrer equation from the broadening of the (101) peak. The morphology and particle size were determined by scanning electron microscopy (SEM) on a JEOL JSM 6700F microscope (Japan). The pore size and porosity were found by the BET method on a Micrometrics ASAP 2000 device (USA) using N₂ adsorption-desorption isotherms at 77 K.

Electrochemical properties of the materials in question were investigated in CR2016 coin cells with a lithium electrode. The working electrodes consisted of 85 % of TiO₂, 10 % of Timcal Super P carbon black and 5 % of a poly(vinylidenedifluoride) binder (PVDF, Solef 6020, Solvay). A dry mixture of TiO₂ and carbon black was gradually added to a solution of PVDF in N-methyl-pyrrolidone (99 %, Aldrich) and stirred under the rotation speed of ~2500 rpm. The resulting slurry was cast onto the surface of 50 μm thick aluminum foil using a doctor blade. The cathode tape was dried at 60 °C until complete removal of the solvent and then rolled. Finally, cathodes cut in the form of disks with the area of 2 cm² were dried in vacuum at 120 °C for 6–7 h directly before assembling the cells. The active material load was ≈ 5.5 mg/cm². Celgard 2400 polypropylene film was used as a separator.

Electrolytes were prepared using a mixture of ethylene carbonate (EC, 98%, Aldrich) and dimethyl carbonate (DMC, 99%, Aldrich) taken in the volume ratio of 1:1. LiClO₄ (Synbias, Ukraine) was additionally recrystallized and dried in vacuum at 170 °C for 14 h. LiPF₆ (99.9%, Gelon) and LiN(CF₃SO₂)₂, (LiTFSI, 99%, Aldrich) were also dried in vacuum before the preparation of solutions. The lithium salt concentration in electrolyte solution was 1 mol/L. All works on electrolyte preparation and cell assembling were carried out in dry glove boxes.

The electrical conductivity of the electrolytes was determined in the temperature range of 15–50 °C and calculated on the basis of impedance spectra (Z2000 impedancemeter, Elins, Russia), obtained in the 100-1 kHz frequency range in glass cells with plane-parallel platinum electrodes.

Galvanostatic cycling was carried out at the constant temperature of 25 ± 1 °C on a Neware Battery Testing System (China). Charge/discharge investigations were performed in the voltage ranges of 1.5-2.75 V and 1.0-2.75 V vs. Li/Li⁺ at different current densities, expressed in C units (1 C = 335 mA/g).

Physico-chemical characterization of TiO₂.

According to the XRD data (Fig. 1), all TiO₂ samples have the anatase structure. In all cases, no impurity peaks have been detected. The sample dried at 150 °C is of low crystallinity, as indicated by weak peaks in the respective XRD pattern. Total crystallinity increases with increasing temperature and duration of heating. The crystallite sizes d(101) calculated using the width of the (101) reflections are presented in Table 1. Their values change twice from 5 nm for the dried sample to ~10 nm for the sample treated at 470 °C.

As can be seen from the SEM micrographs (Fig. 2), TiO₂ samples consist of highly aggregated, irregularly shaped nanoparticles. The size of the particles depends on the thermal annealing conditions (temperature and duration) and varies in the range of ~40–80 nm. The particle sizes exceed the crystallite sizes, which means that each particle consists of up to tencrystallites as the result of aggregation of nanoscale crystallites upon heating.
According to the IUPAC classification, nitrogen adsorption-desorption isotherms for the samples can be attributed to type IV isotherms with capillary condensation in mesopores. The calculated values of the specific surface area ($S_{sp}$) and total pore volume ($V_p$) of TiO$_2$ samples greatly depend on the treatment conditions (Table 1). After drying at 150 °C, the specific surface area is 404 m$^2$/g and the pore volume is 0.34 cm$^3$/g. Heat treatment at temperatures up to 470 °C leads to a decrease in the specific surface area and the pore volume to 80 m$^2$/g and 0.152 cm$^3$/g, respectively. At the same time, the pore size increases from 1.7 to 2.75 nm.

### Table 1.

**Crystallite size and surface properties of TiO$_2$ samples**

| Sample          | $d_{(101)}$, nm | $S_{sp}$, m$^2$/g | $V_p$, cm$^3$/g | $R_p$, nm |
|-----------------|-----------------|-------------------|-----------------|----------|
| 150 °C – 10 h   | 5.0             | 404               | 0.340           | 1.7      |
| 350 °C – 4 h    | 7.0             | 174               | 0.264           | 2.2      |
| 350 °C – 26 h   | 8.5             | 125               | 0.230           | 2.65     |
| 350 °C – 40 h   | 8.8             | 113               | 0.225           | 2.7      |
| 470 °C – 6 h    | 9.8             | 80                | 0.152           | 2.75     |
Effect of electrolyte composition on electrochemical properties of TiO\textsubscript{2}. Electrochemical investigations were made for TiO\textsubscript{2} samples thermally treated at 350 °C and 470 °C. The compositions of electrolytes and their specific conductivities are presented in Table 2.

In the first discharge cycles, process of lithium intercalation into the TiO\textsubscript{2} structure are complicated by the electrolyte decomposition and formation of a solid electrolyte interface (SEI). The contribution of side (secondary) reactions depends on the electrolyte composition, cycling voltage range, as well as the surface and structural properties of the electrodes. The quantitative contribution of the side processes to the overall electrochemical process can be determined based on the ratio of the discharge and charge capacities of the first two cycles. The results given in Table 3 demonstrate how the electrolyte composition and the conditions of thermal annealing of TiO\textsubscript{2} affect the ratio of the discharge capacities of the first (Q1) and second (Q2) cycles. The Q1/Q2 ratio in the case of 1M LiClO\textsubscript{4} – EC:DMC electrolyte decreases with an increase in temperature and time of annealing of TiO\textsubscript{2}. The maximum value of Q1/Q2 is characteristic of the sample 350-4. At the same time, the Q1/Q2 ratios obtained with the 1M LiPF\textsubscript{6} – EC:DMC and 1M LiTFSI – EC:DMC electrolytes are significantly lower and practically independent of the heat treatment conditions of TiO\textsubscript{2}.

Table 2

| No | Electrolyte composition     | Specific conductivity, mSm/cm |
|----|------------------------------|-------------------------------|
|    |                             | 15 °C | 25 °C | 40 °C | 50 °C |
| 1  | 1M LiPF\textsubscript{6} – EC:DMC | 9.8   | 12.1  | 15.4  | 17.5  |
| 2  | 1M LiClO\textsubscript{4} – EC:DMC | 7.7   | 9.4   | 12.0  | 13.6  |
| 3  | 1M LiTFSI – EC:DMC           | 7.5   | 9.2   | 11.7  | 13.5  |

Table 3.

Effect of electrolyte composition and thermal annealing conditions on the specific capacity of the first and second cycle

| Sample | Electrolyte composition     | Q1, mAh/g | Q2, mAh/g | Q1/Q2 |
|--------|------------------------------|-----------|-----------|-------|
| 350 °C – 4 h | 1M LiClO\textsubscript{4} – EC:DMC | 186       | 109       | 1.7   |
| 470 °C – 6 h | 1M LiClO\textsubscript{4} – EC:DMC | 163       | 144       | 1.13  |
| 350 °C – 4 h | 1M LiPF\textsubscript{6} – EC:DMC | 172       | 163       | 1.05  |
| 350 °C – 4 h | 1M LiTFSI – EC:DMC           | 160       | 150       | 1.07  |

At cycling voltage range of 2.75–1.5 V

| Sample | Electrolyte composition     | Q1, mAh/g | Q2, mAh/g | Q1/Q2 |
|--------|------------------------------|-----------|-----------|-------|
| 350 °C – 4 h | 1M LiClO\textsubscript{4} – EC:DMC | 290       | 206       | 1.41  |
| 350 °C – 4 h | 1M LiPF\textsubscript{6} – EC:DMC | 266       | 224       | 1.19  |
| 470 °C – 6 h | 1M LiPF\textsubscript{6} – EC:DMC | 246       | 219       | 1.12  |

At cycling voltage range of 2.75–1.0 V
The charge-discharge curves of the 10th cycle registered in different electrolytes are shown in Fig. 3. The points on the curves corresponding to quasi-equilibrium voltage obtained after 2 hours of relaxation, represent open circuit voltage (OCV). The curves have three main parts corresponding to different stages of lithium intercalation [5, 8, 15, 16].

The first part of the discharge curve (before a plateau at ~1.75 V) is associated with the formation of SEI. It is assumed that in this voltage range, there is no formation of new phases and the \( x \) value in \( \text{Li}_x \text{TiO}_2 \) compound is less than 0.028 [14]. In accordance with our results, the value of \( x \) does not exceed 0.03.

The plateau on the discharge curve at the voltage of ~1.75 V corresponds to the formation of a \( \text{Li}_x \text{TiO}_2 \) compound (where \( x < 0.5 \)) with the theoretical specific capacity of 167.5 mAh/g. However, practically, the value of \( x \) depends on the morphology and structural characteristics of \( \text{TiO}_2 \) particles and, as a rule, does not exceed ~0.4 [14]. The authors [14] suggest that the discharge in this voltage region is determined by the simultaneous presence of the initial \( \text{TiO}_2 \) phase and an orthorhombic \( \text{Li}_x \text{TiO}_2 \) phase formed during discharge. The process limiting the kinetics of the discharge is associated with the limited access of lithium ions to the surface of \( \text{TiO}_2 \) as a result of formation of \( \text{Li}_x \text{TiO}_2 \) structure. Therefore, a decrease in the particle size of \( \text{TiO}_2 \) is considered as the main factor contributing to an increase in the specific capacity. That is, the smaller the particle sizes, the higher the specific capacity of \( \text{TiO}_2 \). It is believed that when the \( \text{Li}_x \text{TiO}_2 \) layer thickness is more than 3-4 nm, the discharge rate is significantly inhibited and the specific capacity decreases [14].

The discharge in the 1.7-1.0 V voltage range is associated with filling of remaining octahedral sites and formation of the \( \text{Li}_x \text{TiO}_2 \) \((x>0.5)\) compound [17]. At the voltage below 1.7 V, the discharge curve represents a sloping curve without pronounced voltage plateau. The specific capacity value of \( \text{TiO}_2 \) in this region is determined by both structural and surface factors (crystallite size and specific surface) and the properties of the SEI formed. The first two factors depend on the conditions of the synthesis of \( \text{TiO}_2 \) and the third is determined not only by the surface and structural properties of \( \text{TiO}_2 \) but also by the properties of the electrolyte [14, 18-21].
The hysteresis existing between the corresponding charge and discharge curves slightly depends on the electrolyte composition. In all cases, when the concentration of lithium ions in $\text{Li}_x\text{TiO}_2$ increases from $\sim 0.36$ to $\sim 0.6$, the magnitude of hysteresis also increases. Depending on the electrolyte composition, the difference in the values of quasi-equilibrium voltage in the lithium concentration range of $0.03$–$0.36$ is no more than $6$ mV.

The 350–4 TiO$_2$ samples have higher sensitivity to the LiClO$_4$-containing electrolyte manifesting a significant decrease of the specific capacity at the second cycle in comparison with the first cycle, even at the relatively low current density (40 mA/g), Table 3.

The decrease in capacity is due to a significant increase in cell internal resistance, which was determined by software for cycling, according to the voltage drop when the discharge current was turned on. So, on cycling in the voltage range of 1.5–2.75 V, the cell resistance values at the first and second cycles for different samples changed from 178 to 293 Ohm for 350–4 sample, from 150 to 216 Ohm for 350–26 sample, from 150 to 208 Ohm for 350–40 sample and from 95 to 131 Ohm for 470–6 sample. After approximately 5–6 cycles, the cell resistance decreases up to 120–140 Ohm and is very close for all the studied samples. As a result, the specific capacity increases and remains stable during further cycling. Similar results have been published previously by two of us [12].

In more detail, the effect of the electrolyte composition on the change of specific capacity from the cycle number and current density is shown in Fig. 4. In the cycling voltages range of 1.5–2.75 V (Fig. 4a), the specific capacity remains stable for all electrolyte compositions. However, when the discharge voltage decreases to 1.0 V, the specific capacity decreases noticeably faster in the case of LiClO$_4$-containing electrolyte (Fig. 4b).
specific capacity on the discharge current density is shown in Fig. 4c. The minimum capacity loss with a change of current density from 40 to 400 mA/g is obtained in 1M LiPF$_6$ – EC:DMC whose specific conductivity is the highest (Table 2).

**Quasi-equilibrium voltage and kinetic characteristics of TiO$_2$.** Fig. 5 shows the discharge-charge curves and the values of the quasi-equilibrium voltage obtained for 350–4 and 470–6 samples in different electrolytes. These curves do not differ from those discussed previously (Fig. 2). However, the specific capacity of 470–6 sample obtained on the voltage plateau of 1.75 V is approximately 10% higher than that of the sample 350–4, and the difference in the values of quasi-equilibrium voltages is not more than 6 mV.

![Fig. 5. Discharge-charge curves of 350-4 and 470-6 TiO$_2$ samples at the current density of 40 mA/g in electrolytes (a) 1M LiPF$_6$ – EC:DMC and (b) 1M LiClO$_4$ – EC:DMC. Points indicate quasi-equilibrium voltage values.](https://ucj.org.ua)

Fig. 5 shows the dependences of specific capacity of TiO$_2$ on cycle number and discharge current density obtained in 1M LiClO$_4$–EC:DMC electrolyte upon cycling in different voltage ranges. The specific capacity during cycling in the voltage range of 2.75–1.5 V is quite stable for all TiO$_2$ samples. When the discharge voltage decreases to 1.0 V, the specific capacity of the 350-4 sample decreases more significantly (Fig. 6 c).

When samples are cycled within a voltage range of 1–2.75 V at the current density of 40 mA/g, the specific capacity is practically independent of the conditions of thermal annealing of TiO$_2$ (Fig. 7a). However, at current density of 400 mA/g, the specific capacity of 350–4
and 470–6 samples decreases by 50 and 25 %, respectively. We suppose that this may be due to the difference in the resistance of SEI, whose properties affect the charge transfer resistance.

The thermal annealing conditions of TiO$_2$ and the resistance occurring in Li-TiO$_2$ cells, we have analyzed the impedance spectra obtained at the resistance occurring in Li-TiO$_2$ cells, we have analyzed the impedance spectra obtained at the various stages of discharge. To this end, TiO$_2$ samples have been taken with maximum and minimum specific surface area, 350–4 and 470–6, respectively. Fig. 8 shows the impedance hodographs in the Nyquist coordinates obtained at the various stages of discharge of Li-TiO$_2$ cells with 1M LiPF$_6$ – EC:DMC electrolyte. The impedance spectra for almost all discharge stages consist of two incomplete semicircles at high and medium frequencies and an almost straight line at low-frequencies. The presence of two semicircles in the high-frequency region indicates the formation of inhomogeneous layers with different conductivities or diffusion rates. The radii of semicircles, which are responsible for the resistance of the real and imaginary parts of the impedance for samples 350–4 and 470–6 are significantly different.

The resistance $R_{\text{min}}$ is basically equal to the sum of the resistances of the electrolyte layer, separator and the interface between the porous electrode and current collector. The $R_{\text{min}}$ value obtained for two samples do not differ significantly and are practically constant over the whole discharge process. The authors [22] believe that the semicircle obtained in the high-frequency region corresponds to a parallel combination of resistance and capacity of the SEI and determine the migration rate of lithium ions in its surface layer. Thus, it can be assumed that the difference in the resistance of the semicircles in the high-frequency region may be ascribed to differences in the structure of the SEI whose properties depend on the surface properties of the samples.

Impedance spectroscopy of Li-TiO$_2$ cells. In order to determine a relationship between

**Fig. 6.** Dependences of specific capacity of different TiO$_2$ samples on the cycle number (a) and discharge current density (b) during the cycling in the voltage range of 1.5–2.75 V and (c) on the cycle number during the cycling in the voltage range of 1.0–2.75 V. Electrolyte – 1M LiClO$_4$ – EC:DMC.
Fig. 7. Dependences of specific capacity of different TiO$_2$ samples on the cycle number (a) and discharge current density (b) during the cycling in the voltage range of 1.0-2.75 V. Electrolyte – 1M LiPF$_6$ – EC:DMC.

Fig. 8 Impedance spectra of Li-TiO$_2$ cells at the various stages of discharge with TiO$_2$ samples 350–4 (a) and 470–6 (b). Electrolyte – 1M LiPF$_6$ – EC:DMC.

The dependence of the resistance of the active part of impedance and OCV on the state of discharge is shown in Fig. 9. The resistance values were determined at the frequency of 0.1 Hz. The greatest difference of the resistance obtained for fully charged cells ($Q_{dch} = 0$) and in a case of 350–4 sample its value is about 5 times higher than for 470–6 sample, where-
in the OCV values practically do not differ. However, after discharge to the capacity of 40 mAh/g, the resistance of both cells decreases and then does not change significantly within the discharge plate of 1.75 V. The closest both in character and resistance are the spectra obtained after the formation of Li$_x$TiO$_2$ ($x>0.5$), suggesting that the diffusion rate at the end of the discharge is determined by the conductivity of Li$_x$TiO$_2$ phase.

![Graph showing the resistance of the active part of impedance and OCV at different stages of discharge](image)

**Fig. 9.** Dependences of the resistance of the active part of impedance and OCV at different stages of discharge

CONCLUSIONS. In this paper, results of the investigation of structural, surface, thermodynamic and kinetic characteristics of titanium dioxide obtained by alkaline hydrolysis are presented. According to XRD and SEM data, TiO$_2$ samples have the anatase structure and consist of highly aggregated, irregularly shaped nanoparticles of 40–80 nm. The specific surface area of the dried TiO$_2$ sample is 404 m$^2$/g and further heat treatment at 350–470 °C with different duration leads to a gradual decrease in the specific surface area to 80 m$^2$/g.

The thermodynamics and kinetics of lithium intercalation-deintercalation process in TiO$_2$ have been studied in a wide range of current densities at different cycling voltage conditions. The specific capacity and its stability upon cycling at different current loads depend on the electrolyte composition and thermal annealing conditions of TiO$_2$ samples. It is shown that at low current densities, the structural and surface properties almost do not affect the specific capacity of TiO$_2$. The maximum specific capacity upon cycling in the voltage range of 1.0–2.75 V and at the current density of 40 mA/g obtained in 1M LiPF$_6$–EC:DMC electrolyte is ~ 210 mAh/g for both 350–4 and 470–6 TiO$_2$ samples, while the decrease in capacity after 100 cycles is ~ 18%. The kinetics of the discharge process at high current densities is limited by charge transfer in the solid electrolyte interface, whose resistance depends on the specific surface area of TiO$_2$. A decrease in the specific surface of TiO$_2$ promotes the decrease in the charge transfer resistance and results in the increase in specific capacity. At the current density of 400 mA/g, the specific capacities of 145 mAh/g and 80 mAh/g are obtained for TiO$_2$ samples with the specific surface of 80 m$^2$/g (sample 470–6) and 175 m$^2$/g (sample 350–4), respectively.

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У роботі подано результати дослідження структурних, поверхневих, термодинамічних та кінетичних характеристик зразків діоксиду титану, отриманих методом лужного гідролізу з розчинів TiCl₄ і LiOH із наступним термообробленням за різних умов. Показано, що зразки TiO₂ мають структуру анатазу з розмірами кристалітів 5–10 нм. Підвищення температури термооброблення зі 150 °C до 470 °C призводить до зменшення питомої площі поверхні TiO₂ з 404 до 80 м²/г та загального об’єму пор з 0,340 до 0,152 см³/г. Методами гальваностатично- го циклировання та імпедансної спектроскопії досліджено вплив складу електроліту та поверхневих властивостей зразків TiO₂ на їхні питомі, термодинамічні та кінетичні характеристики в комірках з літіевим анодом.

Ключові слова: діоксид титану, питома поверхня, електроліт, твердоелектролітна плівка, квазі-рівноважний потенціал.

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REFERENCES

1. Macklin W.J., Neat R.J. Performance of titanium dioxide-based cathodes in a lithium polymer electrolyte cell. Solid State Ionics. 1992. 53: 694.
2. Lafont U., Carta D., Mountjoy G., Chadwick A.V., Kelder E.M. In situ structural changes upon electrochemical lithium insertion in nanosized anatase TiO$_2$. Physical Chemistry C. 2010. 114: 1372.
3. Du T., Zhang W., Peng H., Jain G. Mesoporous TiO$_2$ spheres/graphene composite as a high-performance anode material for lithium-ion batteries. International Journal of Electrochemical Science. 2018. 13: 6229.
4. Madian M., Eychmüller A., Giebeler L. Current advances in TiO$_2$-based nanostructure electrodes for high performance lithium ion batteries. Batteries. 2018. 4: 7.
5. Wagemaker M., Borghols W.J., Mulder F.M. Large impact of particle size on insertion reactions. A case for anatase Li$_x$TiO$_2$. Journal of the American Chemical Society. 2007. 129: 4323.
6. Jiang C., Wei M., Qi Z., Kudo T., Honma I., Zhou H. Particle size dependence of the lithium storage capability and high rate performance of nanocrystalline anatase TiO$_2$ electrode. Journal of Power Sources. 2007. 166: 239.
7. Wagemaker M., Borghols W.J., van Eck E.R., Kentgens A.P., Kearley G.J., Mulder F.M. The influence of size on phase morphology and Li-ion mobility in nanosized lithiumated anatase TiO$_2$. Chemistry–A European Journal. 2007. 13: 2023.
8. Sudant G., Baudrin E., Larcher D., Tarascon J.M. Electrochemical lithium reactivity with nanotextured anatase-type TiO$_2$. Journal of Materials Chemistry. 2005. 15: 1263.
9. Hu Y.-S., Kienle L., Guo Y.G., Maier J. High lithium electroactivity of nanometer-sized rutile TiO$_2$. Advanced Materials. 2006. 18: 1421.
10. Kavan L., Kalbac M., Zukalova M., Exnar I., Lorenzen V., Nesper R., Graetzel M. Lithium storage in nanostructured TiO$_2$ made by hydrothermal growth. Chemistry of Materials. 2004. 16: 477.
11. El-Deen S.S., Hashem A.M., Ghany A.A., Indris S., Ehrenberg H., Mauger A., Julien C.M. Anatase TiO$_2$ nanoparticles for lithium-ion batteries. Ionics. 2018. 24: 2925.
12. Kirillov S.A., Lisnycha T.V., Chernukhin S.I. Precipitated nanosized titanium dioxide for electrochemical applications. Journal of Power Sources. 2011. 196: 2221.
13. Belak A.A., Wang Y., Van der Ven A. Kinetics of anatase electrodes: the role on ordering, anisotropy, and shape memory effects. Chemistry of Matterials. 2012. 24: 2894.
14. Shen K., Chen H., Klaver F., Mulder F.M., Wagemaker M. Impact of particle size on the non-equilibrium phase transition of lithium-inserted anatase TiO$_2$. Chemistry of Materials. 2014. 26: 1608.
15. Gentili V., Bruttì S., Hardwick L.J., Armstrong A.R., Panero S., Bruce P.G. Lithium insertion into anatase nanotubes. Chemistry of Materials. 2012. 24: 4468.
16. Rai A.K., Anh L.T., Gim J., Mathew V., Kang J., Paul B.J., Song J., Kim J. Simple synthesis and particle size effects of TiO$_2$ nanoparticle anodes for rechargeable lithium ion batteries. Electrochimica Acta. 2013. 90: 112.
17. Morgan B.J., Watson G.W. Role of lithium ordering in the Li$_x$TiO$_2$ anatase $\rightarrow$ titanate
phase transition. The Journal of Physical Chemistry Letters. 2011. 2: 1657.
18. Lafont U., Carta D., Mountjoy G., Chadwick A.V., Kelder E.M. In situ structural changes upon electrochemical lithium insertion in nanosized anatase TiO$_2$. Physical Chemistry C. 2010. 114: 1372.
19. Singh D. P., George A., Kumar R.V., ten Elshof J.E., Wagemaker M. Nanostructured TiO$_2$ anatase micropatterned three-dimensional electrodes for high-performance Li-ion batteries. The Journal of Physical Chemistry C. 2013. 117: 19809.
20. Søndergaard M., Shen Y., Mamakhel A., Marinaro M., Wohlfahrt-Mehrens M., Wonsyld K., Dahl S., Iversen B.B. TiO$_2$ nanoparticles for Li-ion battery anodes: mitigation of growth and irreversible capacity using LiOH and NaOH. Chemistry of Materials. 2015. 27: 119.
21. Madej E., Ventosa E., Klink S., Schuhmann W., La Mantia F. Aging effects of anatase TiO$_2$ nanoparticles in Li-ion batteries. Physical Chemistry Chemical Physics. 2014. 16: 7939.
22. Auer A., Portenkirchner E., Götsch T., Valero-Vidal C., Penner S., Kunze-Liebhäuser J. Preferentially oriented TiO$_2$ nanotubes as anode material for Li-ion batteries: insight into Li-ion storage and lithiation kinetics. ACS Applied Materials & Interfaces. 2017. 9: 36828.

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