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Electrochemical properties of TiS_2 and TiS_2/C composite, irradiated by laser and ultrasound

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Electrochemical behavior after laser irradiation of TiS_2 and its TiS_2/C composite with 50% and 80% of NCM (nanoporous carbon material) content in aqueous electrolyte was investigated. It was shown that for TiS_2 and its TiS_2/C composite the capacitance and Faradaic charge storage mechanisms provide identical contributions to the capacity of corresponding storage devices, while laser irradiation stimulates fast reversible Faradaic reactions that leads to 70% increase of pseudocapacitance contribution into the general capacitance.

It was found that preliminary intercalation of fluorine into the electrode material (using thermal exposure method) significantly increases capacity and Coulomb efficiency of storage devices. In particular, their specific energy value becomes almost 5 times greater than corresponding value for the original electrode material.

Keywords: titanium disulfide, composite, laser irradiation, ultrasound dispersion, NCM.

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Introduction

Sulfides of transition metals and their NCM composites have wide range of usages such as supercapacitors, batteries and electrocatalysis. Composites can also have a well-developed surface, high conductivity, and the ability to undergo fast reversible Faradaic reactions that makes them highly important for the production of supercapacitors (both asymmetric and hybrid). The key areas for improving the parameters of these materials are: determining the proportions of the components, their additional processing with a laser (to stabilize the surface and neutralize free chemical bonds), and ultrasound (physical and chemical effects associated with cavitation, exfoliation of aggregated layers of carbon material to unblock access to them, as well as uniform distribution of transition metal sulfide particles in the composite, reducing the size of nanoparticles and increasing the specific surface area, etc.).

I. Experimental, discussion of the results

Electrochemical studies of titanium disulfide and TiS_2/C composites were carried out using a three-electrode electrochemical cell. TiS_2 and TiS_2/C composites with 50, 80 % NCM (nanoporous carbon material) were used as working electrodes before and after laser treatment. Fig. 1-2 represent the discharge curves for TiS_2/C with different NCM contents before and after laser irradiation, obtained in galvanostatic mode at different discharge current values.

The NCM content in the composite increases the discharge duration (Fig. 1-2) which allows redox reactions to occur more completely and this leads to a specific capacity increase (Table 1) which was calculated by the formula

$$C = \frac{2It}{(U_m - \%\Delta U)m}$$

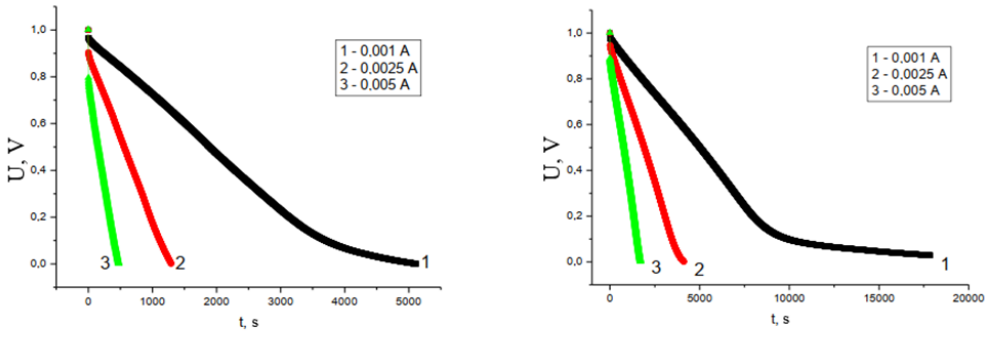


Fig.1. TiS_2/C = 20/80 composite discharge curves before (a) and after (b) laser irradiation.

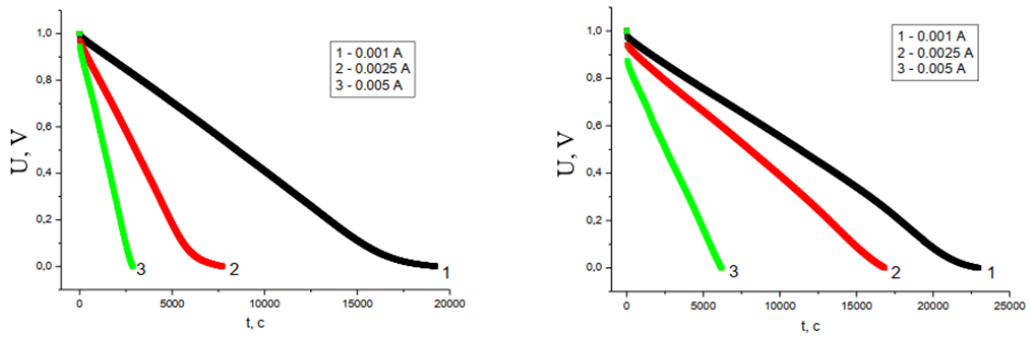


Fig. 2. Discharge curves for the TiS_2/C = 50/50 composite before (a) and after (b) laser irradiation.

Table 1.

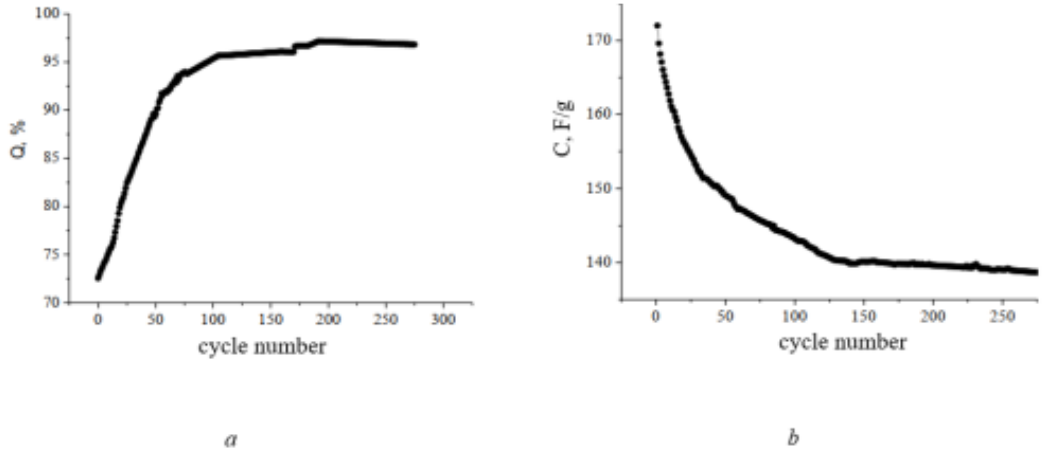
Discharge capacity for TiS2 and laser-irradiated (LI) TiS2/C composites

I, A	C, Ф/г				
	TiS2	TiS2/C=20/80	Laser TiS2/C=20/80	TiS2/C=50/50	Laser TiS2/C=50/50
0.001	47	95	129	165	191
0.0025	28	69	114	149	172
0.005	7	15	95	131	144

where I – charge/discharge current, t – discharge time, m – mass of material, U_m – max voltage, ΔU – voltage drop during discharge (value that defines internal resistance R of the electrode material.) With increasing discharge current the specific capacitance of both pure titanium disulfide and composites decreases. It is due, on the one hand, to the irreversibility of redox reactions at high discharge currents, and on the other hand, to the NCM, in which the discharge current increases along with equivalent series resistance that limited by diffusion in micropores (they limit access to the inner surface of the material.) It was found that the highest specific capacitance (191 F/g) is possessed by the laser-irradiated TiS_2/C=50/50 composite, which is more than 4 times higher than the specific capacitance of pure titanium disulfide.

Thus, the composite where content of TiS_2 and NCM is the same, has the best combination of high carbon conductivity and the possibility of undergoing Faradaic reactions, which are inherent in TiS_2. And laser irradiation stabilizes the developed surface of the composite by neutralizing free chemical bonds, significantly reducing the intensity of irreversible Faradaic reactions and minimizing changes in the working electrode surface structure during the charge/discharge process. Accordingly, this electrode is able to withstand a greater number of cycles without reducing the Coulomb efficiency. Fig. 3 (a) and (b), respectively, do represent the Coulomb efficiency and cyclic stability of this composite for 275 cycles at 2.5 mA current.

In order to determine the intensity of electrochemical reactions, potentiodynamic studies of these materials were carried out at room temperature in the voltage range of –1.0 – 0 V with different scan rates. As can be seen from Fig. 4, voltammogram of pure titanium disulfide has two anodic peaks and one cathodic peak, responsible for the Faradaic reactions occurrence. With increasing scan rate, the anodic peaks shift towards increasing potential, and the cathodic peaks – towards decreasing potential, while their intensity decreases. As is known, the CVA form depends on the scan rate s. Namely, there is a transition from complete reversibility of fast Faradaic processes at $s < s_0$ to partial reversibility at $s \approx s_0$ and to complete irreversibility at $s > s_0$ (s_0 is the critical scan rate below which the processes are reversible). This value is equal to the difference between the charge and discharge peaks and



a *b*

Fig. 3. Dependence of the Coulomb efficiency (a) and specific capacitance (b) on the number of charge/discharge cycles of an electrochemical cell based on laser-irradiated TiS_2/S=50/50 at 2.5 mA discharge current.

should not exceed the value of the equilibrium potential of reversibility, which is determined by the formula:

$$U = \frac{ln2 \cdot R \cdot T}{F}$$

and equals 0.056 V at the room temperature.

As can be seen from Fig. 4: at 1 mV/s scan rate where the difference between the anodic (–0.513 V) and cathodic peaks (–0.558 V) is 0.045 V, the Faradaic processes are reversible. As the scan rate increases, the number of electrolyte ions that are intercalated/deintercalated in the titanium disulfide structure decreases so the processes become partially or completely irreversible.

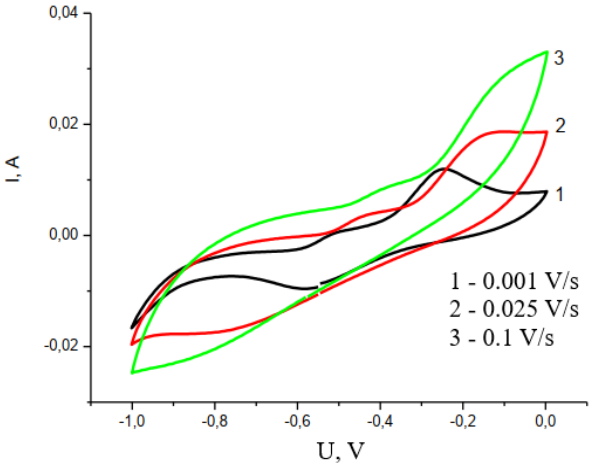


Fig. 4. Potentiodynamic curves for pure TiS_2.

The values of the specific capacitance of the nanocomposite electrodes, estimated from the CVA curves, are given in Table 2.

The dependence of the change in discharge capacity and Coulomb efficiency of the studied materials on the scanning speed is presented in Fig. 5 (a) and (b), respectively.

Nyquist plots (Fig. 6) have semicircular area in the mid-to-high frequency region for all materials, reflecting charge/discharge processes at the electrode-electrolyte interface.

Thus, it can be assumed that for pure TiS_2 and its composite the capacitive and Faradaic mechanisms of charge accumulation make almost the same contribution, while laser irradiation stimulates the fast reversible Faradaic reactions and the contribution of pseudocapacitance can be 65–70% of the total capacitance in this case, according to calculations.

High values of the discharge current and good reversibility of the charge/discharge process are possible due to the current-generating reaction of lithium intercalation into the interlayer space of titanium disulfide [1]:

$$xLi^+ + xe^- + TiS_2 \Leftrightarrow Li_xTiS_2$$

However, such important characteristics as capacity and cycling duration are quite low, since most of the intercalated lithium ions after the first cycles remain localized in the crystal structure between the S–Ti–S layers, and due to the formation of Li_2S and reduction of Ti, the discharge capacity during cycling decreases sharply [2].

To ensure high specific energy of lithium power sources (LPS), mixed cointercalation technologies were used, the essence of which is the preliminary introduction of fluorine into the cathode-active material (TiS_2) by thermal exposure, and the current-generating reaction was provided by its electrochemical intercalation with lithium. The exposure duration was 30 and 60 min. at temperatures of 298 and 573 K, respectively.

It is established that the fluorination regimes significantly affect the thermodynamics of subsequent intercalation by lithium cations. It is seen from Fig. 7 that an increase in the amount of introduced fluorine increases the degree of lithium guest loading during discharge to 1.5 V, while simultaneously changing the functional dependence of the change in Gibbs energy G(x) on the lithium loading. Considering the concentration behavior of the entropy of dissolution (ΔS) of Li in $Li_xTiS_2F_y$ (Fig. 8), the maximum of the differential capacitance in the vicinity of x = 0.75 can be associated with a second-order phase transition in the guest subsystem induced by fluorine.

The nature of the Nyquist diagrams for $Li_xTiS_2F_y$ cointercalation compounds as a function of x is alternately

Table 2.

The value of the charge and discharge capacitances of nanocomposite electrodes based on TiS_2 and TiS_2/C

Scan speed, V/s	TiS_2		TiS_2/C=20/80		Laser TiS_2/C=20/80		TiS_2/C=50/50		Laser TiS_2/C=50/50	
	C_c, F/g	C_d, F/g	C_c, F/g	C_d, F/g	C_c, F/g	C_d, F/g	C_c, F/g	C_d, F/g	C_c, F/g	C_d, F/g
0.001	74	71	118	106	142	0.001	74	71	118	106
0.005			108	93	124	0.005			108	93
0.025	35	32	36	30	40	0.025	35	32	36	30
0.075			23	16	24	0.075			23	16
0.1	7	5	17	13	21	0.1	7	5	17	13

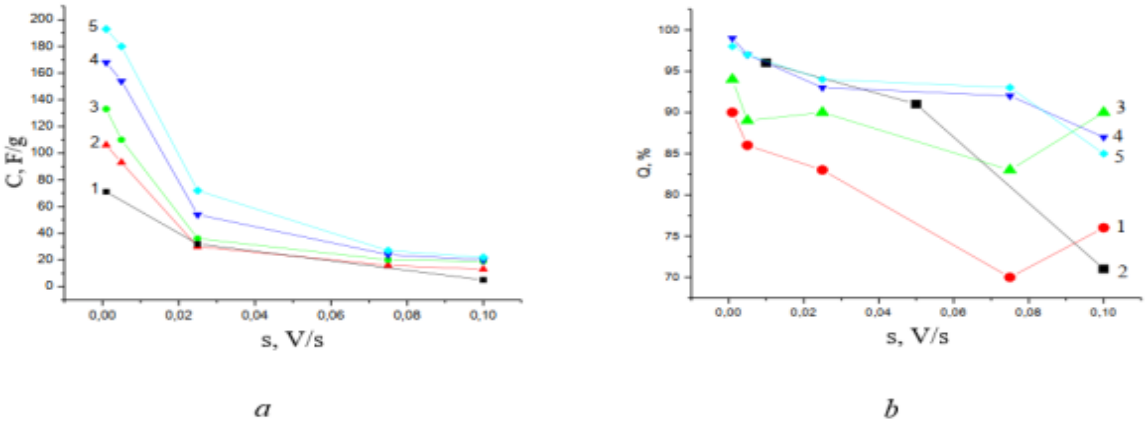


Fig. 5. Dependence of the change in discharge capacity (a) and Coulomb efficiency (b) of the studied samples on the scanning speed: 1 – TiS_2, 2 – TiS_2/C=20/80, 3 – laser-irradiated composite TiS_2/C=20/80, 4 – TiS_2/C=50/50, 5 – laser-irradiated composite TiS_2/C=50/50).

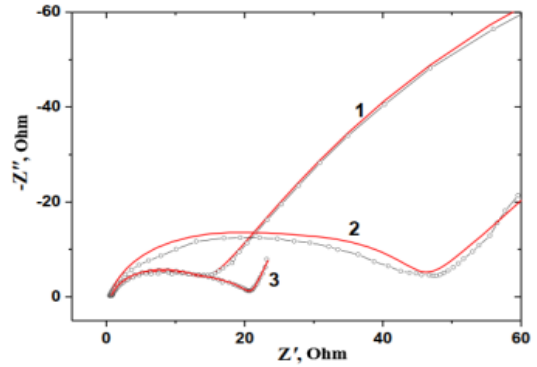


Fig. 6. Nyquist diagrams for electrochemical systems based on TiS_2 (1), TiS_2/C (2) and laser-irradiated TiS_2/C composite (3); dots – experiment, line – simulation result.

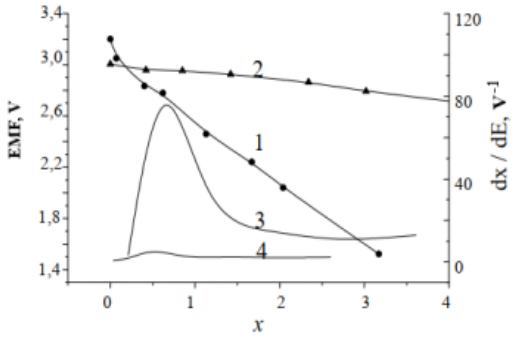


Fig. 7. EMF (1.2) and *dx/d*(EMF) (3.4) as a function of the amount of Li introduced into TiS_2 after its fluorination at 298 K, 30 minutes (1.4) and 573 K, 60 minutes (2.3).

modeled by the Randles–Erschler scheme (for x = 0.25 in particular) and its modified version (x = 0.17; x = 0.66) (Fig. 9) in accordance with diffusion processes that obey the classical and non-ideal Fick laws.

In addition to achieving a high specific energy, there remains the problem of high power increase. To solve it, we have proposed an approach based on modifying the cathode material's band spectrum by laser irradiation with modes that provide an increase in the density of states of delocalized current carriers. It was found that after laser irradiation studied materials reduce their R_{ct} resistance of the charge transfer stage during lithium intercalation in TiS_2F_y by more than 1.5 times. An energy density doubling of laser irradiation for intercalation compounds with strong oxidizing agents ($Li_xTiS_2F_y$) leads to a further (almost threefold) decrease in the charge transfer stage resistance R_{ct} and a change in the kinetic mechanisms: from linear semi-infinite diffusion to the particles motion in the host material (in accordance with the non-ideal Fick law).

As can be seen from Fig. 10, two plateaus are observed in the discharge curves at 1.8 V and 0.7 V potentials that most likely reflect Li^+ ions intercalation into the octahedral positions of titanium disulfide with Li_xTiS_2 formation and Ti^{4+} to Ti^{3+} transition and the intercalant's subsequent entry into Li_xTiS_2 tetrahedral positions with Ti^{3+} to Ti^{2+} reduction. The direction of the discharge curves for the composites in the potential range of 1.8–0.7 V and below 0.7 V indicates the presence of a capacity associated with the EDL polarization, which is due first of all to the structure and morphological features of the obtained material.

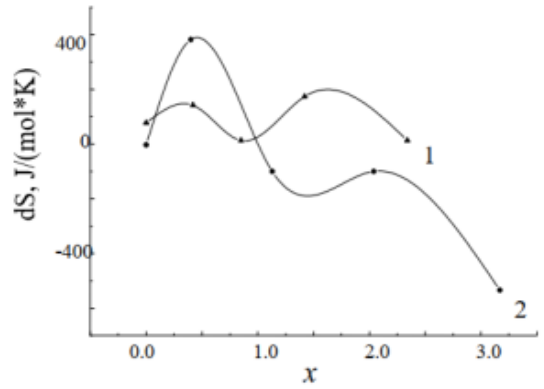


Fig. 8. – Entropy of Li dissolution in $Li_xTiS_2F_y$ as a function of x after fluorination of TiS_2 at 298 K, 30 minutes (1) and 573 K, 60 minutes (2).

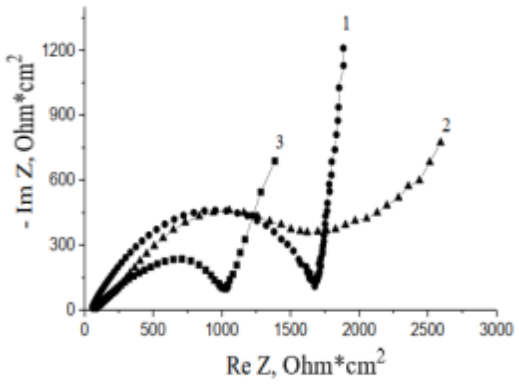


Fig. 9. Nyquist diagrams for $Li_{0.17}TiS_2$<F> (1), $Li_{0.25}TiS_2$<F> (2), $Li_{0.66}TiS_2$<F> (3). Fluorination at 573 K for 60 minutes.

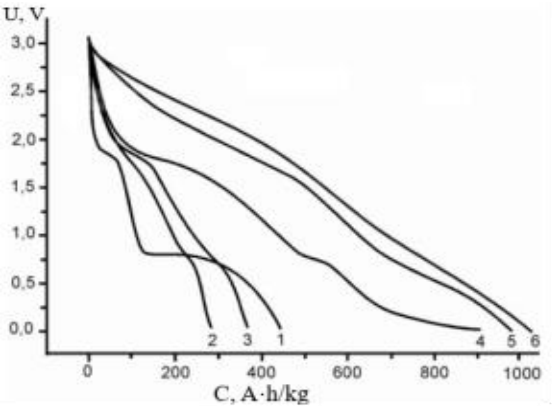


Fig. 10. Discharge curves during the first cycle at a discharge current of 0.3C for LPS with cathode materials:
1 – TiS_2, 2 – TiS_2/C=20/80, 3 – TiS_2/C=80/20,
4 – TiS_2/C=50/50, 5 – laser-irradiated TiS_2/C=50/50,
6 – TiS_2/C=50/50 obtained by ultrasonic dispersion.

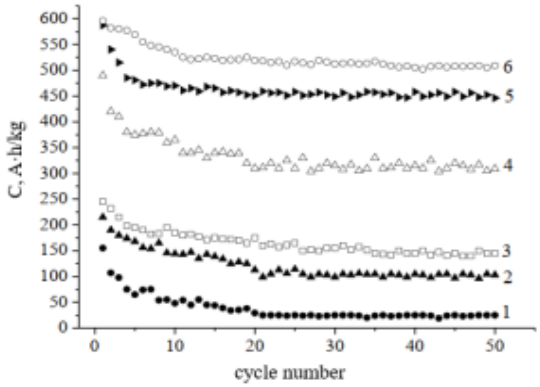


Fig. 11. Dependence of specific capacitance on cycling at a current density of 0.3C for:
1 – TiS_2, 2 – TiS_2/C=20/80, 3 – TiS_2/C=80/20,
4 – TiS_2/C=50/50, 5 – laser-irradiated TiS_2/C=50/50,
6 – TiS_2/C=50/50 exposed to ultrasound.

Composites exposed to laser irradiation and ultrasound (Fig. 10, curves 5, 6) are characterized by specific capacitance's increase, that is probably due to the growing quantity of transport channels in the NCM initiated by laser irradiation and ultrasound.

From the obtained data, it was established that the laser-irradiated TiS_2/C=50/50 composite and the composite obtained by ultrasonic dispersion in acetonitrile (Table 3) form LPS with highest specific characteristics. Their specific capacity is almost four times greater than the specific capacity of LPS formed on the basis of pure TiS_2.

As can be seen from Fig. 11, the specific capacitance for laser-irradiated TiS_2/C=50/50, having reached the maximum value (587 A·h/kg) during the first cycle, gradually decreases and stabilizes after the fifth cycle at ~ 460 A·h/kg, and for the TiS_2/C composite obtained by ultrasonic dispersion, the stable value of the specific capacitance is 525 A·h/kg.

Accordingly, the specific energy during the first cycle is 1057 and 1073 W·h/kg, which is almost 5 times higher than the same value for pure titanium disulfide. Such high specific capacitive and energy characteristics derive from the optimal content of components (that form an electrically connected nanostructure) and successfully selected modes of their modification. In addition, NCM presence in the composite dramatically increases the electrical conductivity. Thus, the synergistic effect of structural ordering after mechanochemical mixing of components and the action of laser irradiation or ultrasound plays an important role in increasing the specific capacitive and energy characteristics of the composite. [3]

Table 3.

Discharge characteristics of LPS based on TiS_2/C composite

#	Material	Specific capacitance *C*, A·h/kg	Specific energy *E*, W·h/kg
1	TiS_2	155	233
2	TiS_2/C=20/80	215	387
3	TiS_2/C=80/20	245	441
4	TiS_2/C=50/50	490	882
5	Laser irradiated TiS_2/C=50/50	587	1057
6	TiS_2/C=50/50, ultrasound in acetone	596	1073

In order to study the electrochemical characteristics of energy storage devices, hybrid cells were formed, with positive electrodes formed with TiS_2/C = 50/50 composites obtained by ultrasonic dispersion in water and acetonitrile and by the mechanochemical method after exposure to laser irradiation, and the negative electrodes were NCM placed in a 33% KOH solution. The mass of the mixture for the positive and negative electrodes was 75 mg and 150 mg, respectively.

On the discharge curves of the studied systems (Fig. 12), taken at currents of 10, 20, and 50 mA, plateaus are observed that are responsible for the passage of fast reversible redox processes, and for composites obtained by ultrasonic dispersion, such processes occur at two potentials (~ 0.85 and 0.4 V), while for the composite obtained by the mechanochemical method, only one plateau is observed at ~ 0.87 V, and the shape of their discharge curves becomes more similar to a straight line, inherent in the capacitive nature of charge accumulation.

As can be seen from Table 4, high values of specific capacitance at 0.01 A discharge current are characterized by HCs (hybrid capacitors), the electrode materials of which are TiS_2/C=50/50 composites, subjected to laser radiation and ultrasonic treatment in acetonitrile (271 and 276 F/g, respectively, at 0.01 A discharge current), while the value of specific energy is 24 and 25 W·h/kg. With 0.05 A increase in the discharge current, the value of the discharge specific capacitance decreases by ~ 1.4 times, while the power increases by 5 times.

Thus, ultrasonic dispersion and laser irradiation, as methods of obtaining and modifying composites, leading to an improvement in the specific characteristics of HCs created on their basis, are promising methods for their further practical application.

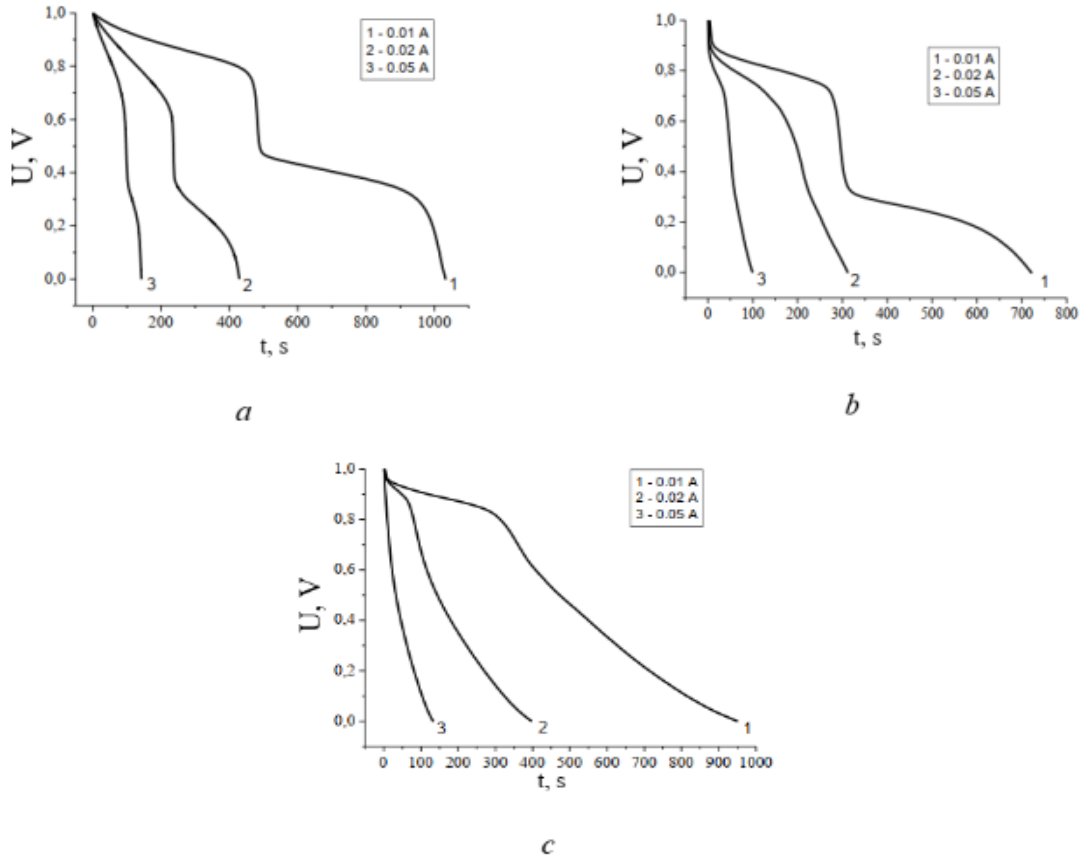


Fig. 12. Discharge curves of a hybrid capacitor with a positive electrode: a – TiS_2/C = 50/50 composite obtained by ultrasonic dispersion in acetonitrile, b – TiS_2/C = 50/50 composite obtained by ultrasonic dispersion in water, c – laser-irradiated TiS_2/C = 50/50 composite obtained by the mechanochemical method.

Table 4.

Specific characteristics of HC based on TiS_2/C composite

Material		Specific capacitance C, F/g			Specific energy E, W·h/kg			Specific power P, W/kg		
	I_d, A	**0.01**	**0.02**	**0.05**	**0.01**	**0.02**	**0.05**	**0.01**	**0.02**	**0.05**
TiS_2/C=50/50, acetonitrile		276	229	191	25	20	17	84	169	428
TiS_2/C=50/50, water		214	185	147	19	16	13	95	189	466
TiS_2/C=50/50, mechanochemical mix, laser irradiated		271	229	189	24	20	17	91	182	453

Conclusions

1. It is shown that the same content of TiS_2 and NCM in the storage device electrodes combines high conductivity and the possibility of rapid reversible Faradaic reactions. At the same time, laser irradiation stabilizes the developed surface of the composite by neutralizing free chemical bonds.

2. By using mixed cointercalation technologies (basically the preliminary introduction of fluorine into the electrode material by thermal exposure method), the degree of lithium guest loading was increased during the device discharge to 1.5V, simultaneously changing the functional dependence of the Gibbs energy G(x) on the degree of lithium loading. In this case, the concentration dependence of the entropy ΔS of lithium dissolution in $Li_xTiS_2F_y$ indicates that the differential capacitance's maximum is reached around x = 0.75.

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Електрохімічні властивості TiS_2 та композиту TiS_2/C, модифікованих лазерним опроміненням і ультразвуковим диспергуванням

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Досліджена електрохімічна поведінка дисульфіду титану, його композиту TiS_2/C з 50% і 80% вмісту нанопористого вуглецевого матеріалу у водному електроліті після лазерного опромінення. Показано, що для TiS_2 і композиту TiS_2/C ємнісний і фарадеївський механізми накопичення заряду вносять практично однаковий вклад в ємність відповідних накопичувальних пристроїв, тоді як лазерне опромінення стимулює проходження швидких оборотних фарадеївських реакцій, що призводить до збільшення вкладу псевдоємності до 70% в загальну ємність.

Виявлено, що попереднє введення фтору в електродний матеріал термічно-експозиційним способом істотно підвищує ємність та кулонівську ефективність накопичувальних пристроїв, зокрема їхня питома енергія майже в 5 разів перевищує дане значення для вихідного електродного матеріалу.

Ключові слова: дисульфід титану, композит, лазерне опромінення, ультразвукове диспергування, НВМ.