Molybdenum Disulfide Obtained by Template Method as an Electrode Material in Electric Energy Storage Devices

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Molybdenum disulfide is obtained by the template method. Its structure and electrochemical properties are investigated. It was found that the working voltage of the LPS for molybdenum disulfide obtained by template method reaches 3 V, the specific capacitance is 180.9 F/g. It was identified that the electric energy storage device the positive electrode of which is molybdenum disulfide obtained by the template method has the discharge specific capacity of 238.9 F/g at a scan rate of 0.001 V/c.

Keywords: Molybdenum disulphide, Template method, Specific capacity.

1. INTRODUCTION

The attention of researchers and consumers is focused on the problem of creating high-efficiency devices for electric power generation, accumulation and conservation. The solution of this problem depends on the properties of the electrode materials which are necessary for electrochemical devices efficient functioning. Along with high conductivity they should possess availability of guest positions, chemical resistance, low cost, environmental safety, low price, etc. Therefore, the search for new materials and modification of the available ones for generating and accumulating devices today is one of the Material Physics' top-priorities.

From this perspective considerable attention is being paid to transition metal dichalcogenides composed of MeX_2 which form layered structures with quadrilateral coupled three-level structures X–M–X held together by the Van der Waals' forces. A vivid representative of such compounds is molybdenum disulfide which along with large specific surface area and guest position for ionic intercalation is characterized by a wide range of oxidation degree from Mo^{2+} to Mo^{6+} in oxidation-reduction reactions. Thus, the electrodes for energy generation, accumulation and storage devices can show both the capacitance of the electric double layer (EDL) and pseudo-capacitance. It is known that theoretical specific capacitance of MOS_2 is approximately 1000 F/g [22].

Under laboratory conditions molybdenum disulfide is obtained by direct interaction of molybdenum with sulfur in the temperature range of 773-923 K in a vacuum. However, such method is hardly suitable due to technological difficulties and inability to monitor morphological characteristics. Therefore, in order to obtain nanostructured MOS_2 other different synthesis and modification methods are applied.

Specifically, electrochemical deposition [31], laser ablation [32], sonochemical method [33], thermal decomposition of ammonium Tetra-molybdates [34], hy-

drothermal method [35], thermal sulphidation [36], solvothermal method [37], template method [38] and creation nanocomposites [0]. However, these methods require additional systematic studies in order to establish the relationships between the mechanisms of reactions, the conditions of their performing, and the properties of the received materials.

Thus, obtaining of nanostructured electrode materials for lithium power sources (LPS) and electrochemical capacitors (ECs), and studying the electrochemical properties of the devices is the main task today.

In this paper, molybdenum disulfide was obtained by the template method; its crystalline structure, morphology and electrochemical properties of energy generation and accumulation devices on its basis were investigated.

2. MATERIALS AND METHODS

A silicate matrix MSM-41 with pore size ~ 3.7 nm was used as a template. To obtain molybdenum disulfide nanoparticles Na_2S aqueous solution was mixed with Li_2MoO_4 and hydrazine aqueous solution. Hydrazine solution was added dropwise to the first solution placed on a magnetic agitator. The template was impregnated by the solution obtained under vacuum ($\sim 10^{-2}$ mmHg), then the solution was placed into the autoclave and heated at 473 K for 24 hours. After cooling in the oven off mode at the room temperature the encapsulated template powder was washed off in isopropanol and dried to its constant weight. Hydrofluoric acid was used to remove template and the MoS_2 precipitation was several times washed off with deionized water and ethanol.

The X-ray diffraction patterns of molybdenum disulfide are obtained by analyzing method and researching the intensity of the X-ray dispersion in $Cu(K_\alpha)$ radiation.

The image of the surface of molybdenum disulfide was obtained on a scanning electron microscope VEGA

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3 TESCAN operating at accelerating voltage of 30 kV.

As stated above it is important to use molybdenum disulfide as the main component for obtaining a composite and then applying it as a cathode material in LPS. To accomplish this the cathode and anode (lithium foil) were placed in a glass weighing bottle with 1 M solution of $LiBF_4$ in γ-butyrolactone, which simultaneously provided the anode/cathode pair's and electrochemical resistance throughout the whole work of the cell. The formation of the electrochemical cell was carried out in the dry weighing bottle in argon atmosphere, in the presence of P_2O_5. The discharge curve was obtained at a galvanostatic discharge of electrochemical cell at a discharge current of 0.3C in the range of potentials of 3-0 V.

At the same time the use of molybdenum disulfide as an electrode material (EM) is no less relevant. Therefore, we implemented a comparative analysis of the characteristics of specific energy used by the hybrid system based on the obtained molybdenum disulfide from which the positive electrode was formed and nanoporous carbon obtained by the method of modified hydrothermal carbonization [114] for a negative electrode. A 33 % aqueous solution of KOH was used as the electrolyte.

A mixture of activated carbon and colloidal carbon in the ratio of 75:25 was used as the basic composition for a hybrid capacitor (HC) negative electrode. Consequently, the mass of the mixture for the positive and negative electrode was 100 and 200 mg. The electrodes for hybrid capacitor with the standard size "2525" were formed on the basis of mixture. Electrochemical studies were carried out using the 8-channel charge/discharge testing bench "Tionid" by galvanostatic and potentiodynamic methods.

3. DISCUSSION OF RESULTS

The X-ray diffractogram of the chemical compound synthesized by the template method (Fig. 1) indicates the obtaining of molybdenum disulfide of a hexagonal bundle (space group P63/mmc, parameters of the elementary cell $a = 0.31631$ nm, $c = 1.22097$ nm, $\gamma = 120$ °); the plane edges and its corresponding angles ratio is shown in Table 1.

As can be seen in the Fig. 2, the surface of the obtained molybdenum disulfide is agglomerated nanoparticles with a diameter of 25-50 nm.
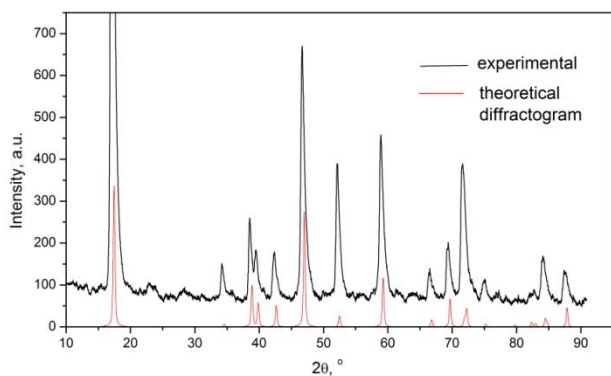

Fig. 1 – X-rays diffraction pattern of MoS_2 obtained by template synthesis

Table 1 – Data from X-ray distraction pattern MoS_2 obtained by template synthesis

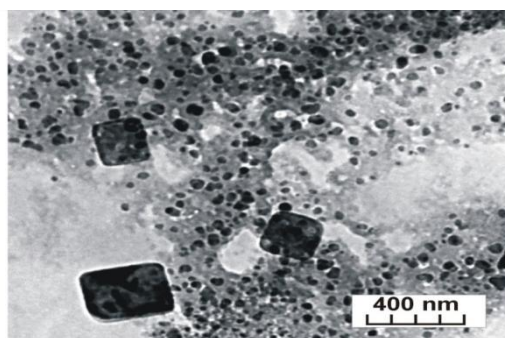| 2θ, °	I/I_0	h k l
17.2668	99.9	0 0 2
34.2072	5.1	0 0 4
39.4882	6.9	1 0 1
42.2972	7.5	1 0 2
46.6494	37.1	1 0 3
52.1086	19.5	1 0 4
58.8838	23.0	1 0 5
66.4308	4.2	1 0 6
69.2766	7.6	1 1 1
71.4810	19.0	1 1 2
74.8618	2.8	1 1 3
84.0256	6.2	2 0 2
87.7369	4.8	2 0 3

Fig. 2 – Microphotography of the surface of MoS2 obtained by template synthesis

Intercalation of lithium ions into molybdenum disulfide is possible due to the higher energy of the valence electronic states of lithium atoms than unfilled by molybdenum cations condition bands in molybdenum disulfide (primarily orbital 4d). And the effect of the increasing of the specific surface area increasing by reducing of the particles size resulted from temple synthesis is expected to remain the powerful factor via the lifespan of the electrode. Lithium ions thereby occupy octahedral vacant positions in the hexagonal crystal since taking up tetra lateral position needs more energy [241]. The transfer of lithium ions into molybdenum disulfide depends not only on the presence of high concentration of charge carriers, vacancies and interstitial areas but also on the low activation energy of the ion jump to form a triple compound Li_xMoS_2. If the guest load of lithium x is less than 0.1 then the lithium ions intercalation into molybdenum disulfide occurs with the minor violations of the host lattice. As the ion concentration of Lithium increases one or more electrons are added to the host phase, forming the ion (MoS_2), which leads to distortion of the octahedral positions of cations of molybdenum, and consequently to significant changes in the electronic structure of the host [24]. Thus, a phase transition occurs (the crystal lattice of molybdenum disulfide transfers from 2H to the 1T phase).

As we can see in the Fig. 3 the discharge curve of the electrochemical cell LPS is close to the ideal and is consistent with the filling of octahedral positions between the layers of molybdenum disulfide that can lead to a phase transition (from 2H to the 1T phase). The emergence of such two-phase area is the result of

strong interaction between ions of lithium and molybdenum disulfide. During such interaction a certain order can arise as much as to the formation of a compound of constant composition equilibrium with the previous phase.
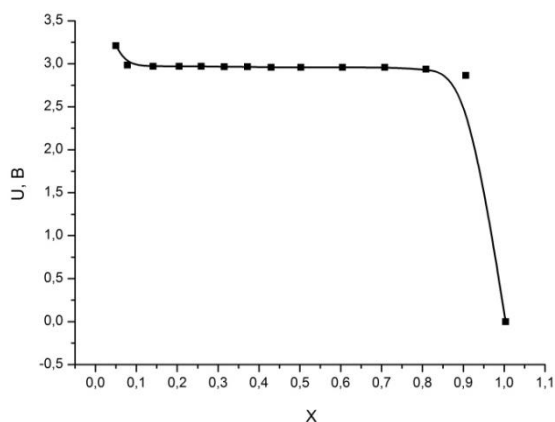

Fig. 3 – Discharge curve of the electrochemical cell LPS with cathode on the base of molybdenum disulfide obtained by template synthesis

At the same time the electrochemical cell discharge specific capacitance is 180.9 F/g.

We created a HC with positive electrodes based on obtained molybdenum disulfide in order to study the electrochemical properties of the electric energy storage devices.

As we can see in the Fig. 4 cyclic voltammograms (CVs) of the hybrid electrochemical cell are characterized by the presence of reversible oxidation-reduction peaks which demonstrates that Faradaic charge accumulation is a specific feature of molybdenum disulfide. Gap-filling of unoccupied orbitals of molybdenum by extranuclear electrons during the discharge of an electrode on the base of MoS2 leads to their valency reduction. At the same time ions of electrolytes get rid of the hydration layer and are absorbed on the surface due to Coulomb interaction. The process will be reversed during the charge. In the meantime, the cyclic voltammograms CVs of the hybrid electrochemical cell have a rectangular shape what indicates the presence and capacitive nature of energy accumulation EDL.
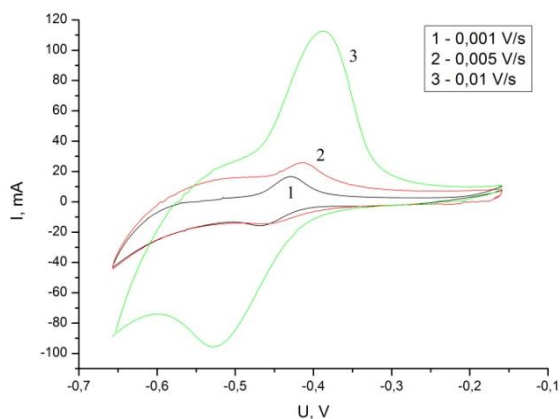

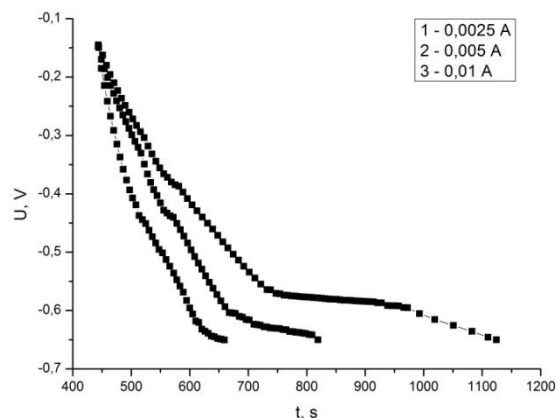**Fig. 4** – CVs HC, with MoS2 obtained by template synthesis as the cathode material

Fig. 5 – Discharge curves HC with MoS_2 obtained by template synthesis as the positive electrode

Such a combination of two mechanisms of energy accumulation from self-organization of nanoparticles in the obtained by the template method molybdenum disulfide leads to high rate of capacitive characteristics in terms of test material (at a scan rate of 0.001 V/c the discharge capacity is 238.9 F/g).

There are some plateaux on the discharge curves of the test material at -0.56, -0.63 V which are responsible for the course of rapid reversible oxidation-reduction processes. At the same time the discharge curves demonstrate the shape very close to the straight line which is typical for the process of charge accumulation due to the formation of EDL. The magnitude of the discharge specific capacitance calculated from the discharge curve at 0.0025 A, is 190.5 F/g which correlates with the obtained magnitudes from cyclic voltammetry.

4. CONCLUSIONS

1. Molybdenum disulfide with hexagonal crystal structure was obtained by template method (space group P63/ mmc, characteristics of the elementary cell $a = 0.31631$ nm and $c = 1.22097$ nm, $\gamma = 120$ º), the surface of which is agglomerated nanoparticles with a diameter of 25-50 nm.

2. It was found that the working voltage of the LPS for molybdenum disulfide obtained by template method reaches 3 V, the specific capacitance is 180.9 F/g, the discharge curve demonstrates the shape very close to the straight line and is consistent with the filling of octahedral positions between the layers of molybdenum disulfide.

3. It was identified that the electric energy storage device the positive electrode of which is molybdenum disulfide obtained by the template method has the discharge specific capacity of 238.9 F/g at a scan rate of 0.001 V/c due to the combination of two mechanisms of energy accumulation due to self-organization of nanoparticles that takes place during the template-based synthesis.

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