

Synthesis and Electrochemical Behavior of the Molybdenum-Modified Electrode Based on Rice Husk

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Article info

Received:
17 February 2017

Received in revised form:
19 May 2017

Accepted:
12 July 2017

Keywords:

Chemically modified electrodes
Voltammetry
Rice husk
Bisorbent
Molybdenum,
Redox processes.

Abstract

The article presents the results of electrochemical studies made on carbon paste electrode based on bisorbents powder modified by molybdenum. Bisorbent consists of carbon and SiO₂. It was synthesized as a support structure obtained from rice husk thermal decomposition products. The obtained sorption material has surface with high specific area – 200 m²/g. Bisorbent was further modified by (NH₄)₆Mo₇O₂₄ · 4H₂O (10 wt.%). The elemental composition of used RH was also determined. The surface morphology of plain and modified BS samples was studied. Recording of voltammetric curves was carried out at pH = 3.80, pH = 6.40 in 0.2 M electrolyte solution of Li₂SO₄. Cathodic and anodic waves were obtained which related to oxidation and reduction processes of molybdenum compounds in the entire range of the potentials (0.8 ÷ -1.2 V). The range of changing molybdate ions concentrations in solution was 2 · 10⁻⁴ ÷ 10⁻² M. The dependencies of kinetic and electrochemical parameters on paramolybdate ions concentration were studied for modified electrode. Nature of changes in molybdenum reduction currents and oxidation currents indicates that Mo⁺⁶ reduction may occur by different mechanisms depending on the composite electrode properties. Results showed the possibility of further the synthesized composite system use for voltammetric determination of low (10⁻⁴–10⁻²) concentrations of Mo₇O₂₄⁶⁻ ions in a solution.

1. Introduction

The studies of electrochemical analysis methods are actively developing due to creation and practical application of chemically modified electrodes. Elaboration of modified electrodes creates new kinds of materials with suitable properties. These electrodes can be widely used in voltammetric sensing, chemical power sources production, electrocatalytic synthesis of organic substances, and in other fields of science and technology.

Nowadays one of the actual problems of electrochemistry is creation of effective sensor systems based on nanomaterials. This kind of material contains stabilized polyvalent metals and their oxides on plant-based sorption matrix [1–3]. The electrodes made of composite materials based on carbon are used in electrocatalytic processes at preparation of different chemical and pharmaceutical products, waste water treatment etc. The rational

use of plant waste can provide sources of sorption materials for the matrix. Considering the tendency to create resource-saving, eco-friendly and non-waste technologies this work has high importance [4–9].

The authors of this study selected rice husk (RH) as a raw material for the composite material and its further modification. RH is an advanced, low cost vegetation waste in Kazakhstan with high sorption properties. The sorption material obtained from the RH has a wide field of application. Some Kazakhstan scientists investigate RH from different regions of Kazakhstan using it mainly as an adsorbent for waste water treatment and similar purposes. [10–15], production of technical silicon [16] or for the supercapacitors [17–18]. All experiments in this study were carried out with RH, taken from the Terenuzek village, Kyzylorda region, Kazakhstan. RH characterized by a high carbon content and amorphous silica content of 15–23%

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with impurities of alkali oxides, alkaline-earth and transition metals up to 4% of the total mineral part content. Such adsorptive materials consisting of two active components (SiO_2/C) are called bisorbents (BS). RH is a high-ash biomass, which is the most suitable precursor for a preparation of porous carbon materials, since it allows to control porosity by mineral part [19–25]. The ions of modifying agent were adsorbed on these carbon-silica materials. Molybdenum ammonium salt $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ is selected as a modifying agent. It is known that the molybdenum compound in oxidation state less than +6 possess catalytic activity in a number of chemical and electrochemical reactions that causes researchers' interest in molybdenum-oxo-compounds [26–32].

In the electrocatalytic systems, the potentials of the electrochemical activity of the catalysts-intermediates are of great importance. These potentials are determined by the following factors: the nature of the modifier, active particles size, catalyzed particles of various nature synergy opportunity etc. In many cases, catalytic systems consist of bi- and tri-metallic inclusions, which are mainly aimed at increasing electrocatalysts efficiency.

This work is devoted to development and investigation of the properties of new modified electrodes based on one kind of Kazakhstan plant waste, which provides low cost raw materials. Modification is done by metal ions of variable valence and their oxides stabilization on the sorption material.

2. Experimental part

In order to receive bisorbent from RH, a weighed sample of raw material was washed 1 time with tap water and at least 3 times with distilled water and then filtered and dried for complete moisture removal at ambient temperature. Then RH was carbonized at 500 °C in inert surrounding (Ar) for 2 hours in order to obtain the sorption material. It is composed of amorphous silica and carbon. Specific surface of annealed RH was determined by BET method (Brunauer-Emmett-Teller); it was 200 m^2/g , pore specific volume was 0.1 cm^3/g and average pore size was within 1.0 ÷ 2.0 nm. Measurements were carried out using SORBTOMETR-M device.

Modification of synthesized BS was done by impregnation method. Salt solution $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was placed on the matrix obtained from RH. After drying, the powder was subjected to heat treatment in argon and hydrogen surrounding ($P = 0.04 \text{ MPa}$) at a temperature of 500 °C. This

was done in order to receive Mo reduced forms and its oxides. Modifier's mass concentration in the samples was approximately 10%.

The surface morphology of the obtained modified material was studied by optical microscope (Leica DM 6000 M) and scanning electron microscope (Quanta 200i 3D) with an integrated Energy Dispersive X-ray analysis (EDAX). Elemental analysis was performed by the FOCUS-2M X-ray fluorescence spectrometer.

Electrochemical studies were performed using the universal potentiostat-galvanostat Autolab PG-STAT 302N series with computer data processing by «NOVA» software. Before measurements the electrolyte was purged with argon for deaeration. The conditions of experiments were chosen according to the similar studies [17–18]. A standard three-electrode cell with modified composite electrode as working electrode was used, as reference electrode silver chloride electrode was used, and as counter-electrode – graphite rod ($d = 0.5 \text{ cm}$, $l = 5 \text{ cm}$). The solution of 0.2 $\text{M Li}_2\text{SO}_4$ was used as electrolyte. Stabilization of the electrode potential occurred 10–15 min after the working electrode immersion in the electrolyte influenced by the speed of inert gas purging through the system. All measurements were performed at 25 °C. The scan rate was 5 mV/s and 10 mV/s .

3. Results and discussion

Figure 1 shows an image of the RH surface after thermal treatment at a temperature of 500 °C in inert argon surrounding. It can be seen from the Fig. 1a that the annealed husk particles have a porous structure, the pores can be divided into large (diameter of 8–10 μm) and small (diameter of 3–5 μm) fractions. The surface of the unmodified BS is presented on the Fig. 1b, c, which also confirms that the structure of the BS is characterized by the presence of macro- and mesopores with predominance of hemispherical and tunnel forms of different sizes. The formation of pores may be caused by the organic part of husk temperature treatment, which leads to formation of the pyrolysis product amorphous structure.

The RH elemental composition is determined by the X-ray fluorescence analysis. C, Fe, Cu, Zn, Mn, Cr, Ca, K, Ti, Cl, S, Ni, Si were found. This fact corresponds to the reference data [10–19]. Unmodified BS samples and composite materials obtained on its base were investigated by EDAX method in order to establish their elemental composition.

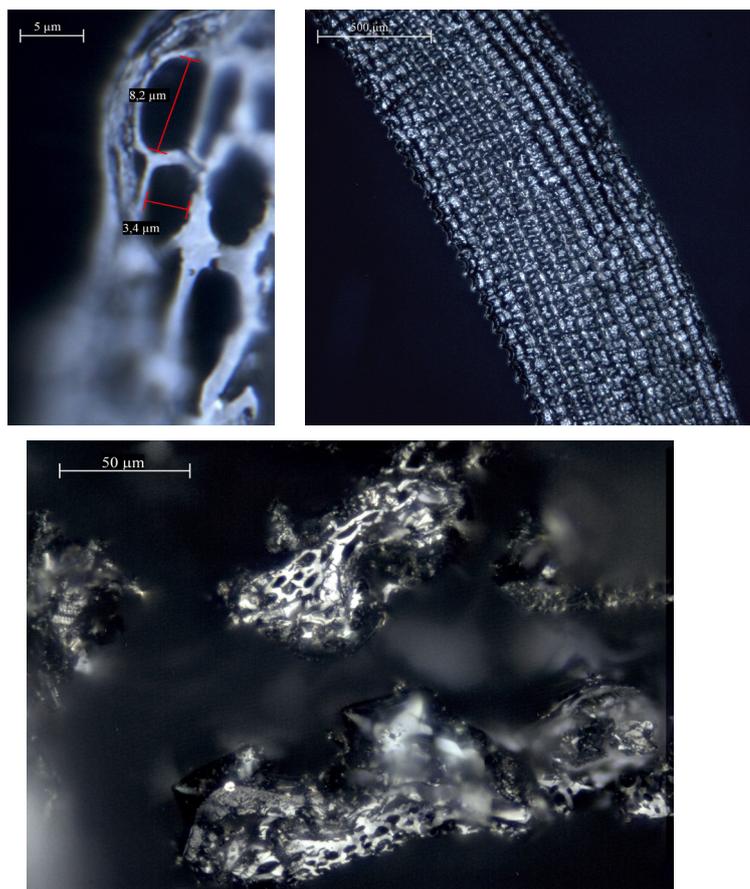


Fig. 1. Microscopic images of the RH surface

According to the results the initial BS is characterized by domination of carbon content comprising 52.12 wt.%, oxygen content of 29.84 wt.% and silicon content comprising 18.04 wt.%. Thus, the obtained RH carbonation product consists of silicon dioxide and carbon-based BS.

After BS sample modification by molybdenum and its reduction, the structure and surface morphology of the materials changed. It was confirmed by the results of scanning electron microscopy (Fig. 2).

The plain surface of carbonized RH (Fig. 2a) consists of fragments and different porous particles with variable size from 2 to 100 μm. Comparing to unmodified sample the modified material (Fig. 2b) is more homogeneous and, apparently, due to repeated thermal exposure it has greater degree of BS destruction. This causes a decrease in the upper limit of the average particle size to 20 μm. One can notice a relatively uniform distribution of the modifying agent on the RH carbonized particles surface.

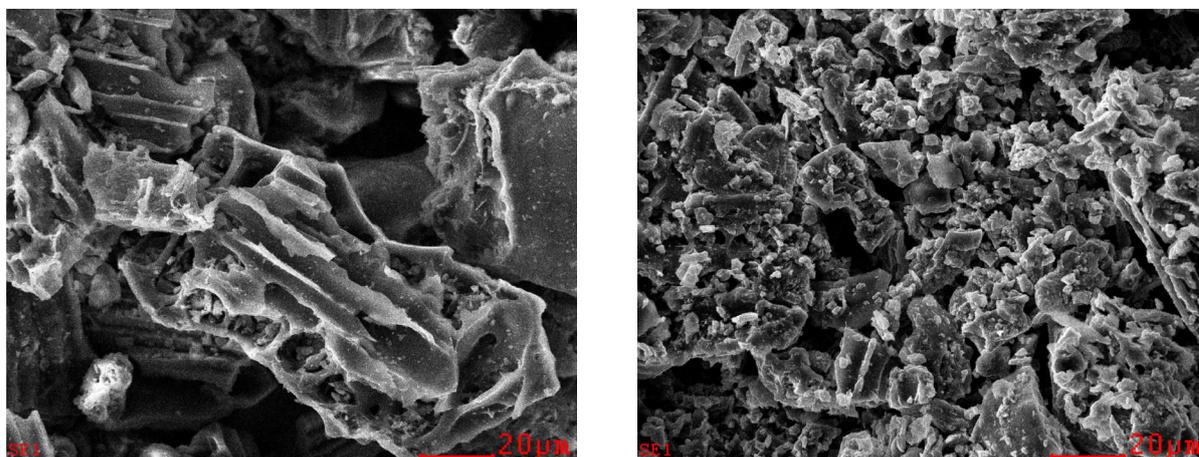


Fig. 2. Surface morphology of carbonized RH and sample modified by Mo (10 wt.%).

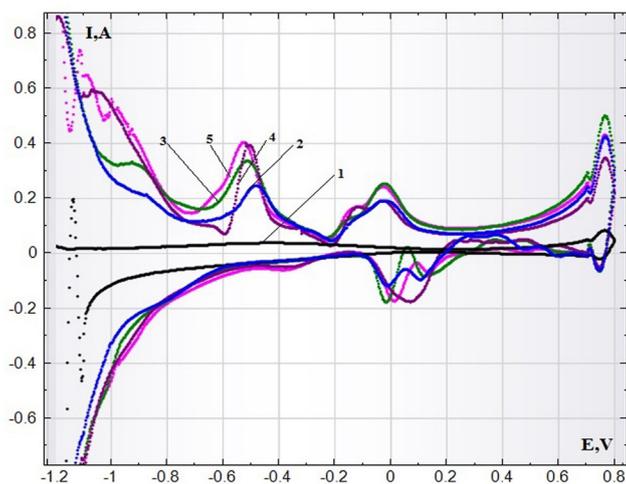


Fig. 3. DVA curves for composite electrode depending on the concentration of $Mo_7O_{24}^{6-}$ -ions:

- 1 – Electrolyte – 0.2 M Li_2SO_4 ; 2 – $C_{Mo_7O_{24}^{6-}} = 2 \cdot 10^{-4}$ M;
 3 – $C_{Mo_7O_{24}^{6-}} = 4 \cdot 10^{-4}$ M; 4 – $C_{Mo_7O_{24}^{6-}} = 8 \cdot 10^{-4}$ M;
 5 – $C_{Mo_7O_{24}^{6-}} = 1 \cdot 10^{-2}$ M, pH = 3.8; V = 10 mV/s.

Figure 3 shows the differential voltammetric curves (DVA) obtained on the carbon paste electrode based on RH. The cathodic and anodic waves were investigated in the entire range of potentials (0.8 – -1.2 V) on the voltammetric curves recorded at pH = 3.80 in 0.2 M Li_2SO_4 . They are associated with the oxidation and reduction processes of molybdenum compounds depending on the paramolybdate ions concentration in the solution. DVA-curves were obtained with a pretreatment of 60 s, at cathode potential value ($E_c = -1.2$ V). The scan rate of the potential in anode direction was $V = 10$ mV/s. The interval of paramolybdate ions concentration change in the solution was $C_{Mo_7O_{24}^{6-}} = 2 \cdot 10^{-4} - 1 \cdot 10^{-2}$ M. From the Fig. 3 it can be seen that with increase of $Mo_7O_{24}^{6-}$ -ions concentration the character and shape of the DVA curves changes. The intensity of current rose and the oxidation and reduction potentials corresponding to the molybdenum compounds shifted to the negative direction.

As a part of the study of the obtained modified materials electrochemical characteristics, series of experiments were performed. These experiments aimed to find out the dependence of the current maximum on the concentration of paramolybdate ions at potentials corresponding to the oxidation waves of the paramolybdate ions in reduced form. Similar dependences were also obtained for electrochemical processes that occur during cathodic polarization of the electrode at $E_c = -0.4$ (Fig. 4).

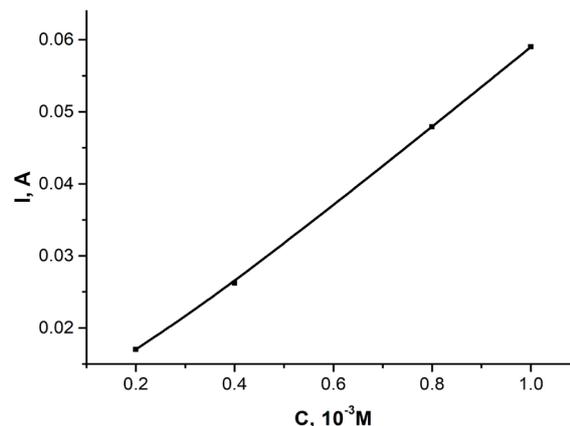


Fig. 4. The dependence of cathodic reduction currents peaks on $Mo_7O_{24}^{6-}$ concentration:

Electrolyte – 0.2 M Li_2SO_4 ; pH=3.8; V = 5 mV/s; $E_c = -0.4$ V.

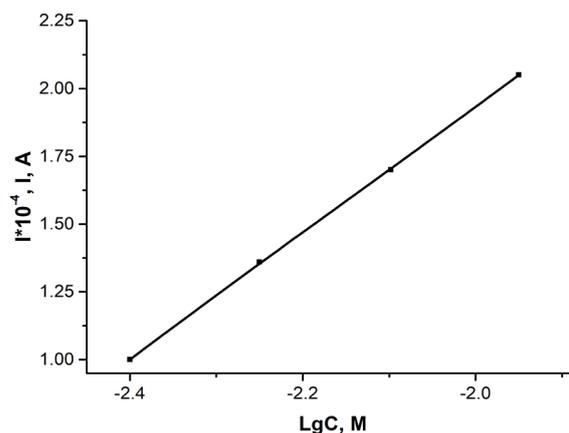


Fig. 5. The dependence of the cathodic reduction current on its concentration: Electrolyte – 0.2 M Li_2SO_4 ; pH = 6.4; V = 10 mV/s, $E = -0.5$ V.

These data indicate that it is possible to determine the concentration of $Mo_7O_{24}^{6-}$ -ions in a solution as a function of the current strength on the molybdenum ions concentration in various oxidation degrees.

One of the most significant features for analysis is the changing nature of characteristics of redox currents in a wide potential range.

According to the Fig. 5 dependence of paramolybdate ions reduction cathodic currents on its concentration $\lg C$ is shown on the cathodic branch of cyclic voltammetry curves (CV) for a composite electrode modified by molybdenum.

Electrochemical behavior of the modified composite material is characterized by the redox poten-

tials of the processes occurring on the electrodes in the presence of depolarizer ions in solution (Fig. 6). Presented electrochemical changes result in the shift of the molybdenum ions reduced forms oxidation potentials and paramolybdate ions reduction process.

According to the Fig. 6a, an assumption can be made about possible change in the nature of the processes influenced by the paramolybdate ions concentration in the solution. This is possible due to the potential change direct dependence on $\lg C$ paramolybdate ions in the solution, moreover, a bend for molybdenum-modified composite is observed. It is related to the dependence of the chemical processes mechanism at the electrodes on the depolarizer concentration. Obviously, at this range of potentials the reduction of Mo^{+6} ions takes place according to different mechanisms depending on the composite electrode nature.

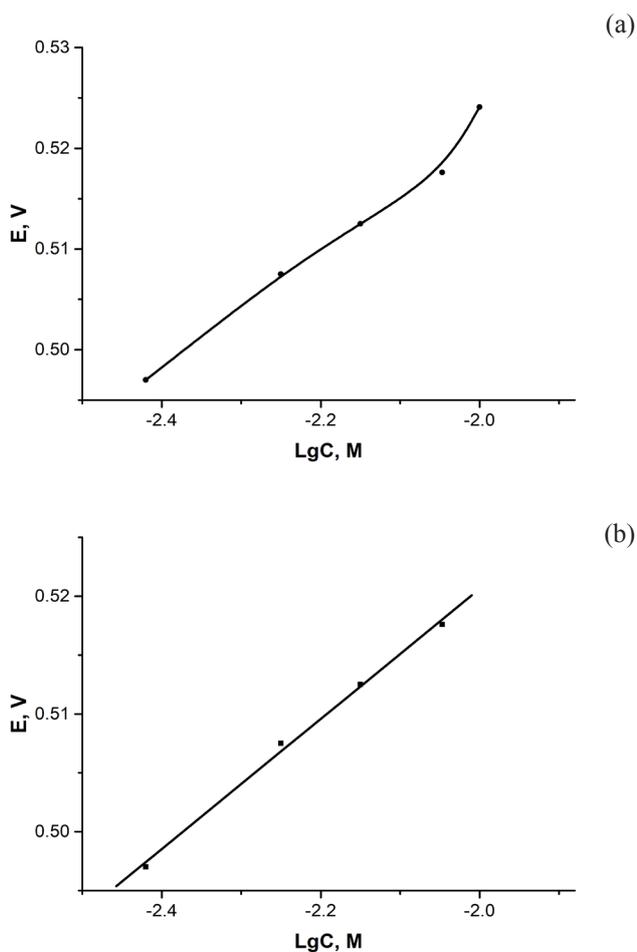


Fig. 6. Dependence of $\text{Mo}_7\text{O}_{24}^{6-}$ – concentration redox potentials displacement in the solution (a) with approximated area (b): Potentials of the process on the anode Electrolyte – 0.2 M Li_2SO_4 ; pH = 6.4; $V = 10$ mV/s, $E = -0.5$ V.

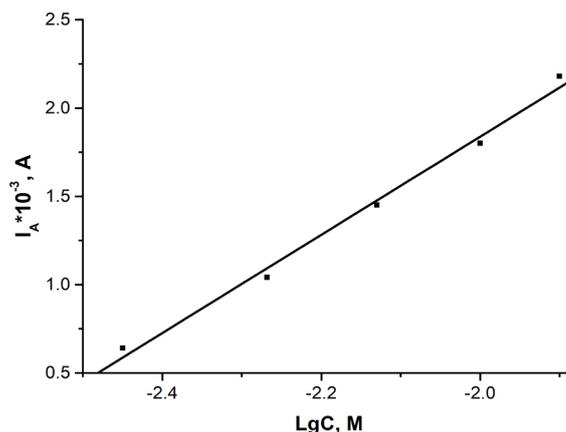


Fig. 7. Dependence of the paramolybdate ions reduced forms anodic oxidation current on the concentration of the solution: Electrolyte – 0.2 M Li_2SO_4 ; pH = 6.4; $V = 10$ mV/s, $E = -0.5$ V.

Nevertheless, it can be seen from the Fig. 6 that a linear dependence is observed in the concentration range $\text{Mo}_7\text{O}_{24}^{6-}$ 0.01–0.007 M, which suggests the possibility of using this molybdenum modified composite electrode material as a sensor for electrochemical determination of Mo^{6+} ions in solutions over the investigated potential range (Fig. 6b). The data approximation was made by the least squares method, the approximation reliability coefficient R^2 is 0.998.

The dependence shown on the Fig. 7 characterizes the impact of the oxidation current of the paramolybdate ions reduced forms on the intensity of the analytical signal at the potential delay in the cathode area of 60 s. The data describe the changing nature of kinetic curves for value of the potential $E = -0.50$ V.

Rate of the reduction reaction can cause bends in the graph, due to the presence of the non-uniform phase and dispersed structure of the initial composite. It is represented by an oxide phase and pre-phase oxide cluster structures in the carrier matrix.

The activity of these compounds regarding chemical interaction with the reducing agents is not the same; moreover, they are reduced at different rates, nevertheless, it does not exclude forming of various oxide phases compounds of molybdenum in specific conditions.

Voltammetric studies with recording of CV curves were carried out which allows to study kinetics properly and determine nature of cathode and anode redox processes. Experiments also were carried out for determination of the analytical

signal intensity as a function of the reduction currents of paramolybdate ions for both unmodified and modified electrodes at different potentials ($E_1 = -0.45$ V; $E_2 = -0.50$ V, $E_3 = -0.55$ V) with the delay in potential of 60 s in the cathode area. The concentration of $Mo_7O_{24}^{6-}$ ions corresponded to the values of $C_{Mo_7O_{24}^{6-}} > 2 \cdot 10^{-4}$ M. During the investigation of composite materials synthesized samples several bends (often two) were clearly noticed on the reaction rates curves of change.

The nature of two transitions of the rates of $Mo_7O_{24}^{6-}$ ions electrochemical reduction can be different; however, in general, it is caused by the nature of electrode reactive surface change. Simpler systems are usually characterized by a smaller number of bends on the kinetic curves under these conditions. The linear sections of the I-IgC dependency suggest the opportunity of their use for analytical purposes.

The obtained experimental data showed the perspective of the synthesized composite electrode based on bisorbents from RH for comprehensive analytical control of a complex system, such as solutions with molybdenum compounds.

4. Conclusions

The RH was studied as a material for creating an adsorption material that acts as a support structure for creating modified electrodes. The structure, elemental composition, specific surface area and pore volume of the obtained BS were determined. BS was modified by $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ to obtain the electrode material.

Dependences of electrochemical parameters on the paramolybdate ions concentration for modified electrodes were studied. The presence of the bend on the curve of E-IgC with paramolybdate ions in the solution for the molybdenum modified composite was detected. Supposedly, this is related to various mechanisms of Mo^{+6} reduction in the potential range of 0.49–0.52 V depending on the composite electrode nature.

A linear dependence was obtained in the $Mo_7O_{24}^{6-}$ ions concentration range of 0.01–0.007 M. Thus, the synthesized composite electrode material can be used as a sensor for electrochemical determination of Mo^{+6} ions in solutions with the range of potentials of 0.49–0.52 V.

According to the research it can be concluded that there is an opportunity to synthesize new electrocatalytic systems based on the products of rice

husk thermal decomposition with further modification by molybdenum ions. Investigation of new electrodes has shown the possibility of their further application in the field of electrochemical sensors, in particular, for the efficient analytical determination of paramolybdate ions in a solution, in case of additional studies of this material.

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