New Electrodes Prepared from Mineral and Plant Raw Materials of Kazakhstan

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Article info

Received:
18 October 2015

Received in revised form:
24 November 2015

Accepted:
15 February 2016

Keywords:
electrode material
shungite rock
carbonization
activation
cyclic voltammetry
carbon containing material

Abstract

Electrode materials were prepared from activated carbonizates of walnut shell, apricot pits and shungite rock from "Bakyrchik" deposit, East Kazakhstan. Physicochemical characteristics of the obtained samples were studied by the Brunauer-Emett-Taylor method, scanning electron microscopy, Raman spectroscopy and other methods. Electrochemical properties of the obtained materials were studied by the method of cyclic voltammetry. It was found that the samples have an amorphous structure. Samples based on plant raw materials after hydrothermal carbonization at 240 °C during 24 h, have more homogeneous and developed surface. Specific surface area of carbon containing materials based on apricot pits is 1300 m^2/g, for those on the based on mineral raw material, it is 153 m^2/g. It was shown that materials after hydrothermal carbonization can be used for catalytic purposes and electrodes after thermal carbonization for analytical and electrocatalytic purposes. Electrode obtained by HTC have electrocatalytic activity. CSC 240 has high background current (slope i/E is 43 mA V^{-1} cm^{-2}), low potential of the hydrogen electroreduction (more positive by ~ 0.5 V than samples based on plant raw materials). The reaction of DA determination is more pronounced on the electrodes obtained by HTC 240 °C, 24 h, due to the nature, carbon structure and high specific surface area of obtained samples.

1. Introduction

Various allotropic forms of carbon are used as electrode materials. There are glassy carbon, powdered graphite, pyrolytic graphite, highly ordered pyrolytic carbon (HOPG), carbon black, carbon fibers, etc., each with specific physical and chemical properties [1]. Compared with metal, carbon electrodes have a lower cost, greater chemical inertness, good electrochemical activity after special treatment, stability at high temperatures, and can be easily modified [2, 3]. Various methods of physical and chemical modification of these materials, giving new properties to nanoscale structures of carbon materials, allow creating new sensors for various applications in biochemistry, ecology and medicine.

At present, there are various methods of carbonization and activation to produce materials with high surface area and pore distribution for use in electrochemistry [4–9]. Carbon containing materials are obtained from various types of raw materials: wood and cellulose [10, 11], peat [12], lignite and hard coal [13], liquid and gaseous hydrocarbons [14], synthetic polymers [15], plant wastes [16] and other raw materials (soot, asphalt, bitumen, tires, PVC and other synthetic polymers waste products, sewage sludge) [17–19].

Electrode materials (EMs) were obtained from carbon-mineral and plant raw materials. Shungite rocks of East Kazakhstan were used as mineral raw material. Shungite rocks are used in metallurgy, chemical industry, in the production of composite materials, as well as sorption material and etc. [20, 21]. The Karelian shungite rocks are the most widely studied. The «Bakyrchik» deposit in East Kazakhstan and the «Koksu» deposit in South-East Kazakhstan are known on the territory of the

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Republic of Kazakhstan. Shungite rocks are very diverse in form of appearance, formation time, genesis and material composition, aggregation and structural state of the carbon component [22]. A group of shungite rocks with silicate mineral base has the most complex composition. Shungite rock of «Bakyrchik» deposit containing aluminosilicates in the mineral component has a good concentratibility, due to this it was decided to study this type of rocks [23, 24].

Walnut shells and apricot pits were used as plant raw materials. They are formed during the processing of fruit, berries and nuts in the southern regions of Kazakhstan and neighboring countries of the Central Asian region.

The novelty of the study is that: wide variety of raw materials types (walnut shell, apricot pits and shungite) and treatment types; elaborated technology of obtaining EMs was adapted to local raw materials; obtained EMs able to compete with the more expensive existing analogues by characteristics (high carbon content, mechanical strength and low ash content) [25–27].

2. Experimental

2.1. Preparation of EM based on shungite rock from «Bakyrchik» deposit

As is known, the raw materials used in technological process should have a constant chemical composition and particle size. Flotation was conducted to stabilize the chemical composition of shungite and to increase carbon content, in the feedstock it is 6–27%. Carbon content in the shungite concentrate was 40 ± 2% by weight after flotation. Flotation and molding of the shungite rock from «Bakyrchik» deposit was done as described in [28].

EMs preparation was performed using carbonization of briquetted material by heat treatment method (TC) (temperature – 700 °C, inert medium – argon, time – 1 h) and hydrothermal treatment (HTC) in an autoclave glass (temperature – 240 °C, medium – H_2O, pressure – 20 bar, time – 24 h). Heteroatoms (oxygen, hydrogen, sulfur, nitrogen, silicon, metals) are removed as gaseous products during the carbonization process. Therefore, carbon content and mechanical strength are increased [29]. Optimal conditions of carbonization were identified in [22, 28, 30].

To increase the specific surface area, carbonated samples were activated using superheated steam in the reactor at the temperature of 800–850 °C for 1 h.

2.2. Preparation of EM based on plant raw materials

The plant material was crushed in «RM-120» rotary knife mill (Vibrotekh, Russian Federation). Next, the raw material was treated by two methods of carbonization – thermal (TC) and hydrothermal (HTC), followed by activation with superheated steam at the conditions similar to those used in the preparation of carbon material (CM) based on carbon-mineral raw materials.

As the result, six types of EM were obtained (Table 1).

Determination of pH of the aqueous extract, ash mass fraction, water mass fraction (moisture), adsorption activity on iodine, strength and specific surface of EM was done as previously described in [24].

2.3. Study of the morphology of EM surface by scanning electron microscopy (SEM)

The surface morphology of the samples was examined using «Quanta 200i 3D» scanning electron microscope (FEI Company, USA) in al-Farabi KazNU National Open-Type Laboratory of Nanotechnology. Samples were fixed in a copper holder using a conductive adhesive paper and scanned at working distance = 9.7 mm and high-voltage = 15.00 kV.

Table 1
Carbon containing electrode materials

Material	Carbonization conditions	Abbreviation
Carbonizate of shungite concentrate	Thermal 700 °C, 1 h	CSC 700
Carbonizate of shungite concentrate	Hydrothermal 240 °C, 24 h	CSC 240
Carbonizate of walnut shell	Thermal 700 °C, 1 h	CWS 700
Carbonizate of walnut shell	Hydrothermal 240 °C, 24 h	CWS 240
Carbonizate of apricot pits	Thermal 700 °C, 1 h	CAP 700
Carbonizate of apricot pits	Hydrothermal 240 °C, 24 h	CAP 240

2.4. Study of the electrochemical behavior of EM

Carbon materials are used for the extraction of the gold and other precious metals from the leaching solution, as well as for the sensor production. Electrochemical properties of the materials were studied using CVA method. The electrolyte was a solution of 0.1 M NaCl + 0.1 M HCl at gold (III) concentration of 1.46 mmol/dm^3. The sweep range was from -1.1 V to 2.2 V. Scan starts from + 0.8 V to the cathode region. Measurements were performed using Nova 302N potentiostat-galvanostat (Autolab, Netherlands) by the method of cyclic voltammetry (CV) in a cell with undivided space. Silver chloride electrode was served as reference electrode, platinum electrode – as auxiliary, the working electrode was made of graphite rod coated with a thin layer of EM paste.

ITO-glass (indium tin oxide) is a semiconductor material based on indium tin oxide. EM applied to ITO-glass were studied at the voltammetric determination of dopamine. Sodium phosphate buffer (pH = 7.4) containing KH_2PO_4, $Na_2HPO_4 \times 7H_2O$, NaCl, H_2O was used for the experiment. Voltammogram of ITO-glass was taken as blank line. Dopamine (DA) (contracted from 3.4-dihydroxyphenethylamine) is an organic chemical. In the brain, DA functions as a neurotransmitter – a chemical released by neurons (nerve cells) to send signals to other nerve cells.

3. Results and discussion

The mechanical strength, adsorption activity of iodine, the pH of the aqueous extract, moisture and ash content is the basic parameters that characterize carbon containing materials.

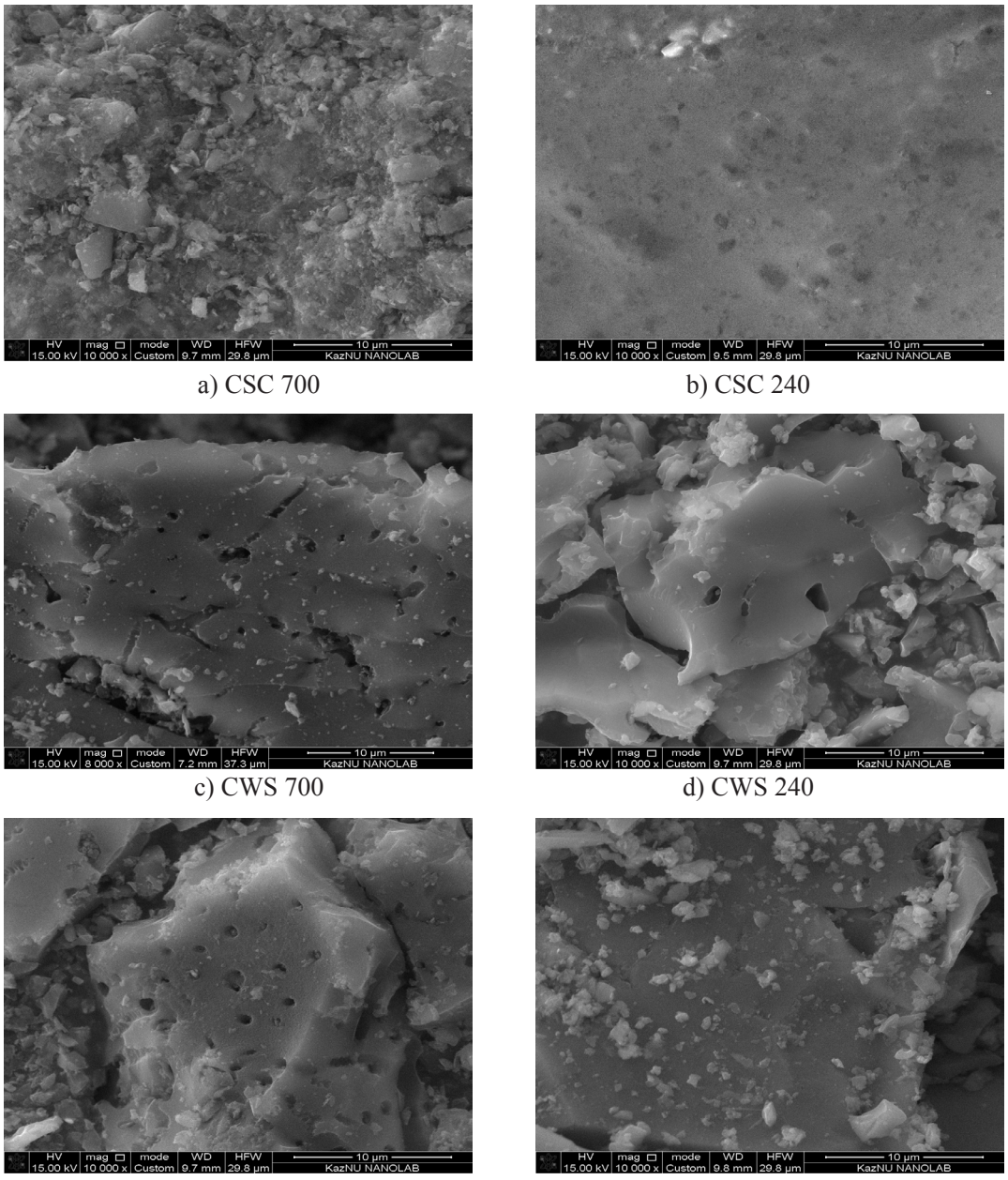
The highest specific surface area is characteristic for EMs based on plant raw materials after hydrothermal carbonization (Table 2). Hydrothermal carbonization results in leaching of lignin-containing compounds, opening the pores, which leads to an increase in specific surface area. Hydronium H_3O^+ is formed as the result of the reaction. During the thermal carbonization (700 °C), there may occur the «blockage» by non-volatile compounds or substances, decomposing at the given temperature, which partially «cleaned» during activation. pH of the aqueous extract of EM based on plant raw materials is shifted to the alkaline side [31]. Samples based on plant raw materials have greater mechanical strength. It is associated with preservation of the natural structure feedstock. A high ash content of the samples based on shungite can be explained by a high content of the mineral component (60%).

Images obtained by scanning electron microscopy show that structure of samples is different (Fig. 1) and confirm the high specific surface of the samples based on plant raw materials. The surface of EMs based on carbon-mineral raw materials represented by heterogeneous structure with local accumulations of acinar (dendrite) and isometric shapes, overlaid (secondary) interspersed and vein textures are widespread. This is due to the presence of secondary minerals – quartz and pyrite. Carbon in EMs has fibrillar microstructure, spongy and globular microstructure microstructures are also found. Size of the individual globules is 2–3 μm. The surface of samples based on plant raw material is more uniform, expressed in the form of porous structure with holes with a diameter of 1–2 μm which is very characteristic for plant tissue [31].

After thermal carbonization (700 °C) and activation, the surface is non-uniform; the particles have irregular shapes and sizes. After hydrothermal treatment, samples had loose and homogeneous surface. Differences in the pore size can be associated with the decomposition of organic substances during the activation process and the nature of the carbon skeleton. A larger number of organic compounds in the samples after hydrothermal carbonization apparently increases the number of pores formed during the activation process.

Table 2
Physicochemical characteristics of the samples

Sample	Specific surface, m^2/g	Adsorption activity of iodine, %	pH of the aqueous extract	Mechanical strength, %	Mechanical strength, % Ash content, %
CSC 700	153	24.6	7.5	53	53.7
CSC 240	129	25.1	7.0	49	67.8
CWS 700	423	59.5	9.1	86	3.8
CWS 240	571	54.3	8.2	75	4.2
CAP 700	506	78.6	8.6	91	3.2
CAP 240	1300	63.5	8.0	83	3.4



a) CSC 700 b) CSC 240

c) CWS 700 d) CWS 240

e) CAP 700 f) CAP 240

Fig. 1. Microstructure of the studied samples.

Raman spectroscopy (Fig. 2) was used to monitor changes in the molecular bonds structure of the obtained EMs. Analysis of the Raman spectra of EMs indicates the presence of two powerful, broad peaks with maxima at about 1350 cm^{-1} and ~1600 cm^{-1}, which characterize the amorphous structure of the samples. These peaks can be attributed to the so-called D (Diamond) and G (Graphite) bands. The spectra of the samples after hydrothermal carbonization show a rise in the high frequency region. This character of Raman spectra is due to the appearance of photoluminescence. Since the method of hydrothermal carbonization comprises treating samples in water, it can be assumed that the luminescence is caused by the saturation of the carbon bonds by hydrogen atoms. Samples based on activated carbonizates of apricot pits are characterized by more intense lines, indicating more ordered structure. These EMs spectra are typical for the structure of all groups of sp^2-atoms in the rings and chains of G peak, as well as for vibrations of sp^2-atoms in the rings and sp^3-hybridization of the carbon atoms of D peak.

Study of Au^{3+} ions behavior on carbon containing electrodes is of interest for analytical chemistry and for gold hydrometallurgy. Polarization curves of EMs based on plant raw materials after hydrothermal treatment are characterized by low background current and wide stability window, -0.8 ÷ 1.3 V for CAP 240 and -0.8 ÷ 1.0 V for CWS 240,

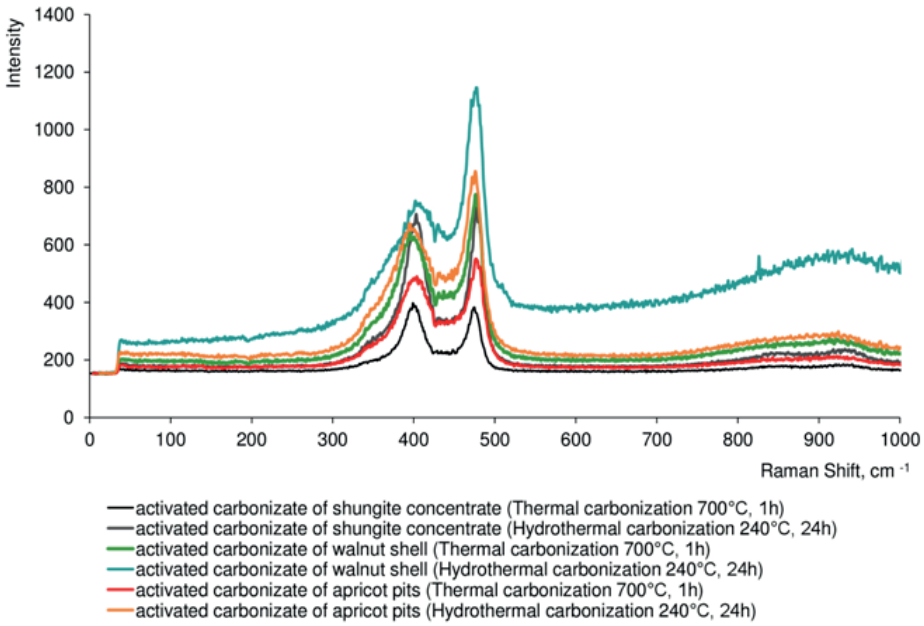


Fig. 2. Raman spectra of carbon containing electrode materials.

the height of the gold reduction peak (+0.45V) for CWS 240 is higher more than 2 times, and the anodic peak of gold dissolution merges with the wave of chlorine formation (Fig. 3). CSC 240 shows a high background current and a narrow potential window -0.3 ÷ 0.6 V. Also there are two anodic peaks at +0.65 V and 1.2 V, which may refer to the formation of the adsorbed oxide of monovalent and trivalent gold.

EM based on shungite demonstrates anodic oxidation peak of the gold at the reverse sweep, judging by the fact that its height is much greater than the cathodic, it can be argued that there is a simultaneous chemical adsorption of gold, along with the cathodic accumulation.

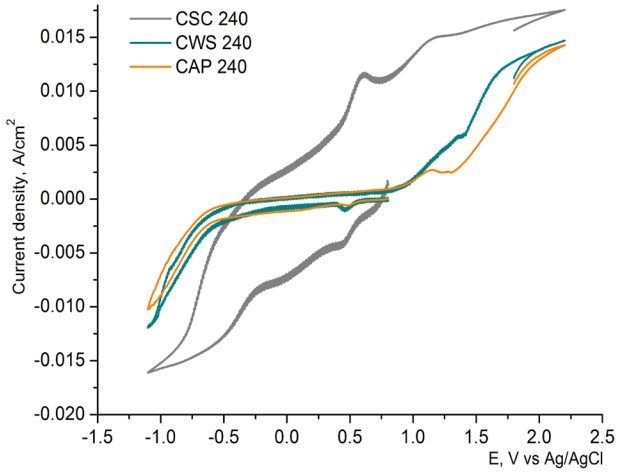


Fig. 3. CVA-curves on the test electrodes obtained by hydrothermal carbonization.

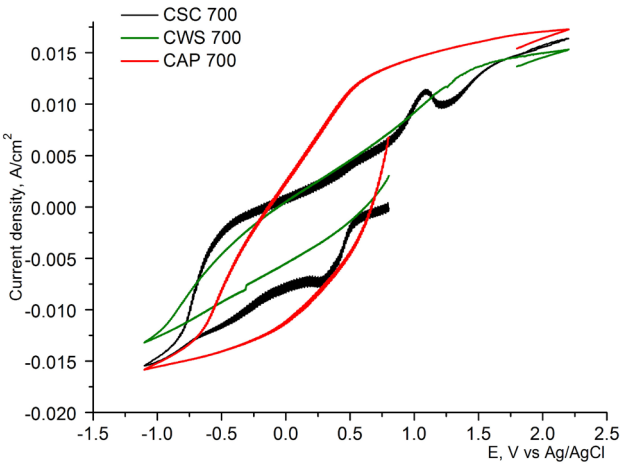


Fig. 4. CVA-curves of the test electrodes obtained by thermal carbonization.

CSC 700 shows oxidation and reduction peaks of the gold ions greater than those of the CSC 240 (Fig. 3), whereas EM based on plant raw materials (CWS 700, CWS 240, CAP 700, CAP 240) are inactive for gold ions (Figs. 3 and 4). The gold cathode peaks is wider for CSC 700 compared with CSC 240, while the anodic peaks are almost not changed. The gold oxidation and reduction signal could not be observed due to high background currents for electrodes after HTC (Fig. 4) for the samples based on plant raw materials.

It was shown that the signal of dopamine oxidation on the carbon nanotube electrode at 0.3 V vs a saturated calomel electrodes (SCE) are increased twenty fold compared to traditional carbon paste

electrode at 0.22 V (from 1 mA to 20 mA) in works [32, 33]. The well-defined reversible peak of the DA electrooxidation is shown on the studied samples at 0.3 V, except CAP 700 (Figs. 5 and 6), the same as on the carbon nanotube electrode. However, DA oxidation current value is much higher – about 50 mA. Two confluent peak of the electroreduction at 0.3 V and 0.52 V are shown on the electrodes after HTC (240 °C, 24 h). The second peak is possibly due to the presence of residual organic impurities.

According to the obtained curves of cyclic voltammograms (Figs. 5 and 6), it can be concluded that the reaction of DA determination is more pronounced on the electrodes obtained by HTC 240 °C, 24 h, peaks are separated clearly. This is due to their higher surface area as compared to CM obtained by TC 700 °C, 1 h.

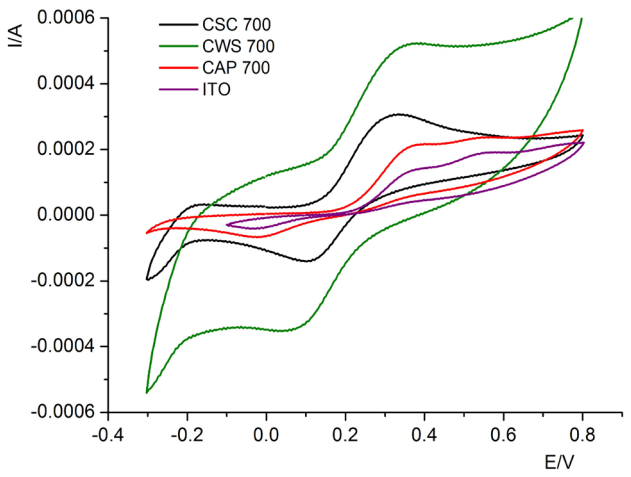


Fig. 5. Cyclic voltammograms of dopamine on the test electrodes obtained by thermal carbonization.

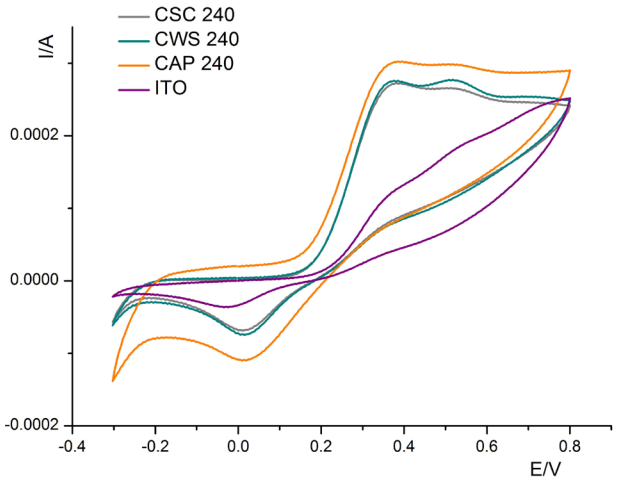


Fig. 6. Cyclic voltammograms of dopamine on the test electrodes obtained by hydrothermal carbonization.

4. Conclusions

Carbon containing materials for electrodes from activated carbonizates of plant raw materials and products of enrichment of shungite rock from «Bakyrchik» (East Kazakhstan) deposit were obtained. Physicochemical properties of obtained materials were studied. Specific surface areas of obtained carbon materials were determined. It was found that the samples after hydrothermal carbonization (240 °C, 24 h) based on plant raw materials have a higher specific surface area (571–1300 m^2/g), in comparison with the samples after heat carbonization at 700 °C for 1 h (423–506 m^2/g). Indicators of adsorption capacity after hydrothermal carbonization range from 25.1 to 63.46%, after heat carbonization – from 24.6 to 78.6%. Mechanical strength of the plant raw material samples is up to 91%. pH of the aqueous extracts of plant materials is shifted to the alkaline side. Ash content of samples from plant material ranges from 3.2 to 4.2%, for samples from mineral raw material – from 53.7 to 67.8%. Samples based on plant raw materials have a more uniform microporous structured surface.

Raman spectroscopy of the samples showed that the samples have two peaks at 1350 cm^{-1} and 600 cm^{-1}, which correspond to D and G bands, respectively. The obtained spectra are typical for groups of atoms having sp^2-hybridization.

Electrode obtained by HTC have electrocatalytic activity. CSC 240 has high background current (slope i/E is 43 mA V^{-1} cm^{-2}), low potential of the hydrogen electroreduction (more positive by ~ 0.5 V than samples based on plant raw materials). CWS 240 and CAP 240 have low potential of the chlorine oxidation in the anode region; CWS 240 is more active. Thereby, EM after HTC (240 °C, 24 h) can be used as a catalytic material; and the electrodes of this type are suitable as the oxidizing mediators to detect substances, which are difficult to oxidize or reduce. Samples based on shungite and plant raw materials after TC (700 °C, 24 h) are promising for analytical and electrocatalytic purposes. The reaction of DA determination is more pronounced on the electrodes obtained by HTC 240 °C, 24 h, due to the nature, carbon structure and high specific surface area of obtained samples.

Acknowledgements

This research was conducted under the scientific and technical program “Fundamental Basis of Processes Based on the Electrochemical Reactions” funded by the Ministry of Education and Science of Kazakhstan.

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