


STUDY OF KAZAKHSTAN'S SHUNGITE AS ELECTROCATALYST SUBSTRATE IN HYDROGEN EVOLUTION REACTION IN ACIDIC MEDIA

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ABSTRACT. The most efficient method to produce hydrogen is by electrolysis of water, and scientist's current research is focused on developing inexpensive catalysts for this process. The article aims to study a carbon material (CM) obtained from shungite raw materials as electrocatalyst support in hydrogen evolution reaction (HER). The obtained activated CM has a multi-layered lamellar morphology with a specific surface area 356.40 m²/g. Electrocatalytical properties of the activated carbon material are the following: overpotential (η) at 10 mA/cm² of 0.515 V vs. RHE with a Tafel slope of 172.5 mV/dec and good stability in acidic media. The obtained results show that activated CM from shungite raw material can be used as an electrocatalyst for obtaining hydrogen.

Keywords: *hydrogen, carbon material, shungite, electrocatalyst, hydrogen evolution reaction.*

INTRODUCTION

Hydrogen is actively studied as an alternative to fossil fuel, due to its high heat value and the environmentally friendly final product, *i.e.*, water [1, 2]. One of

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the ways of obtaining hydrogen is water electrolysis, which is easy, available equipment-wise, and provides high purity of hydrogen without toxic waste. Hydrogen evolution reaction (HER) is the main reaction in water electrolysis and is widely studied with various metals, alloys, and composite materials. Noble metals are considered to be the best options for HER [3,4], due to the low stress of hydrogen. Among those, platinum is considered the best catalyst for the electrochemical production of hydrogen, but economic reasons limit its wider use in HER [5,6]. Palladium can be an electrocatalyst in HER alongside with Pt. As known, nowadays Pd and its alloys are widely used in hydrogen storage.

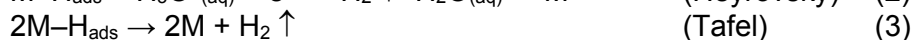
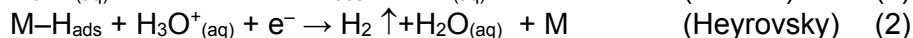
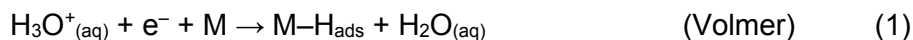
In terms of economic efficiency, several transition metal oxides (Ni, Co, Mn, Fe, etc.) have been extensively studied in HER [7-9]. The main obstacles to the use of metal oxides as electrocatalysts are the interface complexity of the hybrid structures, relatively high resistance, low selectivity and durability, and susceptibility to gas intoxication followed by negative environmental impact. In addition, most metal oxides are semiconductors or dielectrics.

Carbon materials are known to be widely used as electrodes in electrochemical processes. This is due to the fact that carbon has good thermal stability, controlled surface chemical properties, and corrosion resistance against acids and bases. The literature has reported investigations on carbon-based materials such as carbon nanotubes, carbon nanofibers, graphene, activated carbon, and extrinsic carbon structures, as electrodes. [10]. Among all the carbon materials mentioned above, activated carbon is the most prominent due to its cheap and easy production technology, using different available materials (plant-based or carbon-mineral-based), large active surface area, porous structure, and high conductivity, as in the case of metals [11].

The aim of this article is the study of the electrocatalytic activity of carbon materials obtained from shungite solids - waste materials from the processing of polymetallic ores in Kazakhstan [12], for the hydrogen evolution reaction.

RESULTS AND DISCUSSION

In acidic solutions, HER occurs at the surface of the electrode following a multi-step electrochemical reaction:



where: M is a vacant surface site of the electrocatalyst, and the M-H_{ads} is the absorbed hydrogen atoms.

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Briefly, the process consists of an initial discharge of the hydronium ions and the formation of an adsorbed hydrogen intermediates (*i.e.*, $M-H_{ads}$, Volmer reaction 1), followed by the formation of H_2 either in Heyrovsky reaction 2, or in Tafel reaction 3 [13-16].

Three types of materials - shungite solids, flotation concentrate, and activated CM - were selected to investigate the HER, in acidic media. The content of the various elements in these materials is shown in Table 1. It can be seen that after the enrichment process by carbonization and activation, the impurity content decreased significantly.

Table 1. X-ray diffraction element analysis of carbon materials.

| Carbon materials | Element's content, % | | | | | | | |
|-----------------------|----------------------|--------|-------|-------|-------|-------|-------|--------|
| | Mg | Si | P | S | K | Mn | Fe | Al |
| Shungite solids | 0.897 | 26.375 | 0.063 | 0.254 | 3.675 | 0.141 | 8.837 | 10.812 |
| Flotation concentrate | 0.552 | 15.106 | 0.042 | 4.055 | 3.19 | 0.082 | 8.87 | 8.199 |
| Activated CM | 0.201 | 0.00 | 0.099 | 0.030 | 2.241 | 0.046 | 0.417 | 0.00 |

The SEM images of the carbon-based materials (Fig 1) show the shungite solids have a layered lamellar structure, but after the flotation and carbonization processes its surface loses this characteristic layering, becoming noticeably rougher.

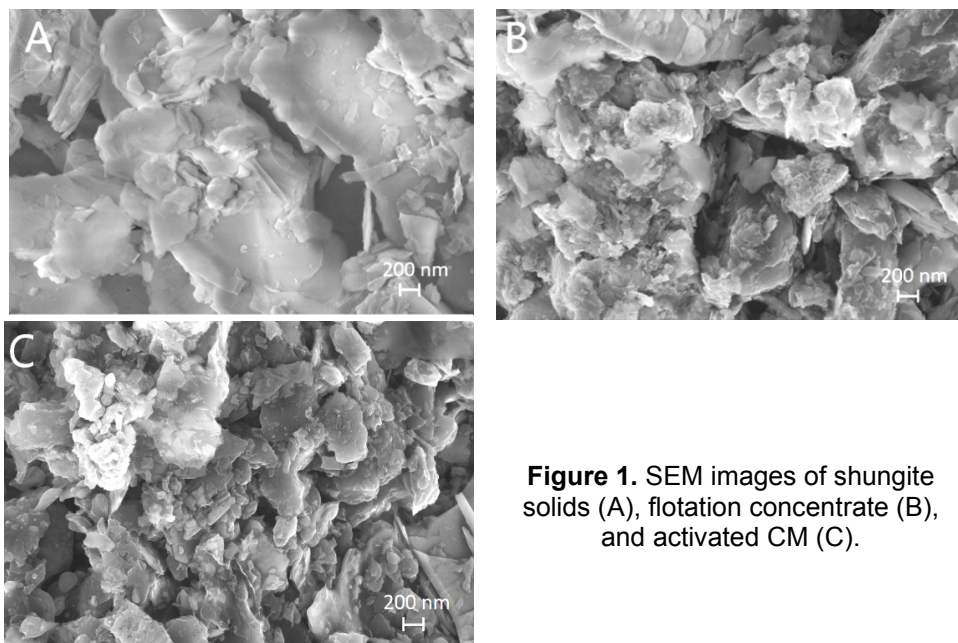


Figure 1. SEM images of shungite solids (A), flotation concentrate (B), and activated CM (C).

As can be seen from the pore distribution curve (Figure 2), after the carbonization and activation step, the porosity of the carbon material increases, and the material is mainly formed by micropores. Table 2 provides the numerical values of the specific surface area and pore volume for the studied carbon materials. In the case of the activated carbon material, the specific surface area (356.4 m²/g) and the pore numbers (0.5 cm³/g) have maximum values.

Table 2. Porosity of carbon materials.

| Carbon materials | Carbon content, % | Specific surface area (S _{BET}), m ² /g | Total pore volume, (V _{tot}), cm ³ /g | Micropores, % |
|-----------------------|-------------------|--|--|---------------|
| Shungite solids | ≥10 | 9.38 | 0.03 | 70.37 |
| Flotation concentrate | 25 | 16.30 | 0.05 | 71.74 |
| Activated CM | 51 | 356.40 | 0.50 | 89.40 |

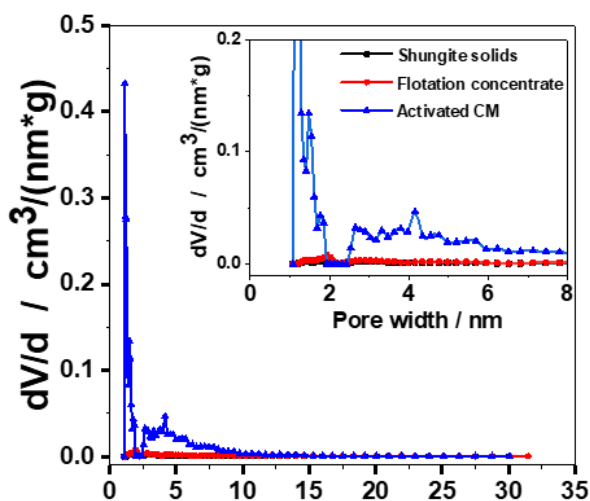


Figure 2. Pore size distribution curve.

The electrochemical activity of carbon materials was studied in an acidic environment of 0.5 M H₂SO₄ at 25°C, by recording linear voltammograms at a scan rate of 10 mV/s. In the HER polarization curves presented in Fig 3, the potential values recorded *versus* Ag|AgCl electrode were converted into potential values expressed *versus* reversible hydrogen electrode (RHE) using the following equation 4 [17]:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E^0_{\text{Ag/AgCl}} + 0,059 \times \text{pH} \quad (4)$$

It is worth mentioning that, in order to be an ideal catalyst for the HER process, the studied material should provide a high current density value for a low overpotential value, as well as a low value of HER onset potential (*i.e.*, on the recorded $j - E$ diagrams, the potential value where the H_2 evolution behavior will be initially observed) [17]. From a practical point of view, the electrocatalytical activity of any material in HER is estimated by comparing the overpotential (η_{HER}) values, recorded at 10 mA/cm^2 .

As seen in Fig 3A, the bare glassy carbon electrode (GCE) has negligible electrocatalytic activity towards HER, while the different studied carbon materials show enhanced electroactivity in HER, probably due to the presence of the active sites in their structure. Also, the values summarized in Table 3 show that the onset potential increases in the following order: -0.8 V vs. RHE (at GCE) $< -0.351 \text{ V vs. RHE}$ (at Flotation concentrate/GCE) $< -0.298 \text{ V vs. RHE}$ (at Activated CM/GCE) $< 0.03 \text{ V vs. RHE}$ (at (Pt/C(10%))/GCE), respectively. At the same time, the studied carbon materials have the following increasing overpotential order, at 10 mA/cm^2 : -0.052 V vs. RHE (at (Pt/C(10%))/GCE) $< -0.515 \text{ V vs. RHE}$ (at Activated CM/GCE) $< -0.602 \text{ V vs. RHE}$ (at Flotation concentrate/GCE), respectively. It must be underlined that the HER overpotential at 10 mA/cm^2 has the lowest value at commercial Pt/C(10%), *i.e.*, -0.052 V vs. RHE , which is comparable to the value reported in the literature for similar electrocatalysts (*e.g.*, -0.040 V vs. RHE at Pt/C(20%)) [17]).

Table 3. Electrocatalytic properties of studied carbon materials.

| Carbon materials | Onset potential, V vs. RHE | η_{HER} recorded at 10 mA/cm^2 , V vs. RHE | Tafel slope, mV/dec |
|------------------------------|-------------------------------|---|------------------------|
| GCE | -0.8 | - | 561.5 |
| Flotation concentrate/GCE | -0.351 | -0.602 | 312.9 |
| Activated CM/GCE | -0.298 | -0.515 | 172.5 |
| (Pt/C(10%))/GCE | 0.03 | -0.052 | 59.3 |

In order to obtain information about the kinetic mechanism of the hydrogen evolution reaction at various electrocatalytic materials, Tafel plots are necessary to be represented (equation 5) [14]:

$$\eta = a + b \times \log |j| \quad (5)$$

where: η is the overpotential, b is the Tafel slope, j is the current density.

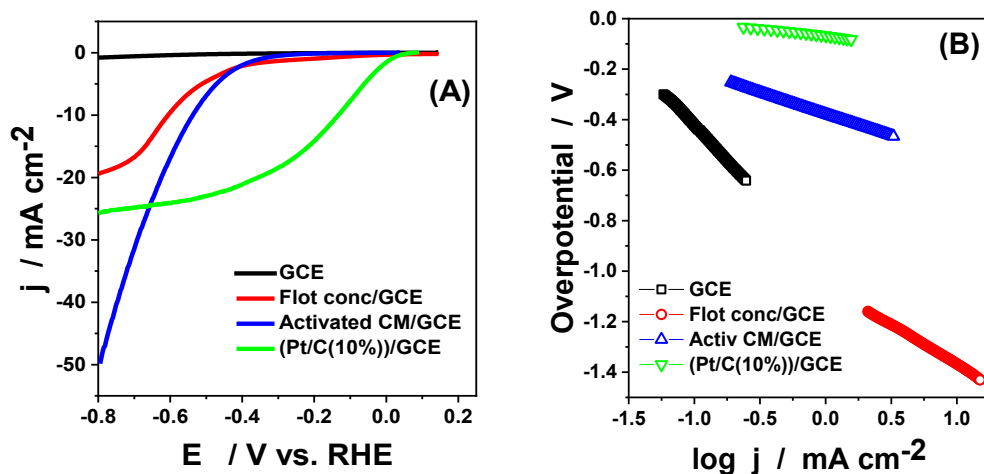


Figure 3. Linear polarization curves (A) and the corresponding Tafel plots (B) for HER at bare GCE (black), flotation concentrate/GCE (red), activated CM/GCE (blue), and (Pt/C(10%))/GCE (green) modified electrodes. Experimental conditions: electrolyte, 0,5 M H₂SO₄; scan rate, 10 mV/s; starting potential, 0.1 V vs. RHE.

Thus, the slopes of the linear portions of the low overpotential values of the LSV polarization curves are estimated and compared.

Moreover, Tafel slope values depend on the overpotential (η) and the surface coverage with M-H_{ads} species for various rate-determining steps of HER [13, 16]. In our case, for Pt-C(10%) the Tafel slope is 59.3 mV/dec, as reported in the literature for similar electrocatalyst (*i.e.*, 34.4 mV/dec at Pt-C(20%) [17]). Also, the Tafel slopes of 172.5 mV/dec (at activated CM) and 312.9 mV/dec (at flotation concentrate), indicate that the activated CM having the lowest value of the slope has a higher HER activity compared with the flotation concentrate material [17]. Moreover, it can be concluded that the kinetic of HER follows steps in which the hydrogen adsorption and desorption occur in consecutive Volmer- Heyrovsky reactions [16, 17] and that the initial proton adsorption (*i.e.*, Volmer reaction 1) is the rate-determining step of the whole HER process [18].

The material's long-term stability is an essential parameter to be estimated for a HER electrocatalyst. Thus, by chronoamperometry at an applied potential of -0.5 V vs. RHE, for a period of 3 hrs, the stability of activated CM was researched. As presented in Figure 4, the activated CM shows acceptable stability; the current density decrease from the initial value was ~30%. Moreover, the linear polarization curves recorded before and after chronoamperometry measurements (Figure 4, inset) showed that there are no significant changes from the initial curve, which suggests good stability of the activated CM material.

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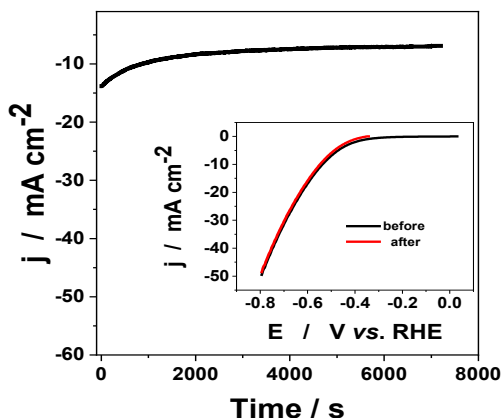


Figure 4. Chronoamperometry curve of activated CM and comparative linear polarization curves of activated CM before and after chronoamperometry measurements (inset).

CONCLUSIONS

Two types of activated carbon materials - flotation concentrate and activated CM - were obtained from shungite solids by froth floatation, followed by carbonization and activation steps. Morphological and structural characteristics of the materials were presented. The electrochemical activity in hydrogen evolution reaction in acidic media was investigated by linear polarization curves, and chronoamperometry. The Tafel slopes showed that the activated CM having the lowest value of the Tafel slope (*i.e.*, 172.5 mV/dec) has a higher HER activity compared with the flotation concentrate material. The long-term stability estimated from LSV before and after chronoamperometric measurements showed good stability of the activated CM material. According to the obtained results, the activated CM made from shungite raw material can be employed as an electrocatalyst to produce hydrogen.

EXPERIMENTAL SECTION

Reagents

The following reagents were used in the present study: shungite solids (from Bakyrchik deposit, East Kazakhstan region), Flotol flotation agent (from KhimProm), kerosene (TC-1 from RPG), Nafion[®] (5% in ethanol, from Sigma

Aldrich), ethanol (95.0 %, from Sigma Aldrich), 0.5 M H₂SO₄ (State Standard 14262-78) and Pt/C (10%) (from Sigma Aldrich).

Preparation of activated CM

The shungite solids having a low content of carbon were enriched by different methods. Shortly, shungite rock was preliminarily crushed, until the final particle size was $\leq 300 \mu\text{m}$. The composition of the initial samples for enrichment was averaged and selected by the quartering method. Shungite materials were ground to $100 \mu\text{m}$ and enriched in carbon content using froth floatation with two-step rewashing, utilizing Flotol floatation agent and kerosene to obtain floatation concentrate samples. In order to obtain activated CM samples and to increase the porosity of the material, the shungite floatation concentrate was treated by carbonization at $700 - 750 \text{ }^\circ\text{C}$, followed by steam-gas activation at $800 - 850 \text{ }^\circ\text{C}$.

Methods of investigation

The morphology of the obtained carbon-based samples was investigated using scanning electron microscopy. Micrographs were obtained using an Ultra-high Resolution Scanning Electron Microscope (UHR FE-SEM Hitachi SU8020). It was equipped with secondary electron detectors, four-quadrant electron backscatter photodiode detector.

The porous characteristics of the materials were obtained using N₂ - sorption experiments, which were carried out using Quadrasorb evo device for volumetric gas sorption. Before analysis, the samples were degassed at $250 \text{ }^\circ\text{C}$ and a pressure of $1 \cdot 10^{-6}$ bar for 12 hours. Specific surface area (S_{Specific}) was determined using the BET equation (Brunauer-Emmett-Teller). The total pore volume (V_{tot}) was calculated based on the nitrogen amount adsorbed at the highest relative pressure.

Electrochemical measurements were performed in a three-electrode cell, equipped with the modified electrode as the working electrode, the Ag|AgCl reference electrode, and a platinum grid as an auxiliary electrode, respectively. The electrolyte was a 0.5 M H₂SO₄ solution. All measurements were carried out using a computer-controlled AUTOLAB (type PGSTAT302N, Methrom, The Netherlands) potentiostat/galvanostat.

Electrode preparation

Modified electrodes based on the immobilization of carbon-based materials in a polymeric matrix were prepared by the drop-casting method.

Thus, 50 mg of carbon-based material were dispersed in 100 μL of Nafion[®] solution (5%) and 50 μL of ethanol (95.0%). The obtained dispersion was ultrasonicated for 30 min. Then, a volume of 10 μL of dispersion was dropped onto the mirror-polished glassy carbon electrode surface (6 mm diameter) and left to dry, at room temperature. The obtained electrodes (symbolized as: flotation concentrate/GCE, activated CM/GCE, (Pt/C)/GCE) were then used for the study of the electrocatalytical activity of the activated carbon material for HER. In order to compare the obtained material's properties, electrodes with commercial catalyst Pt/C (10%) were also prepared.

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