ELECTROCHEMICAL MODIFICATION OF GRAPHITE SURFACE

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Abstract: *Thermodynamic and electrochemical parameters of intercalation and deintercalation of hydrosulfate ions into the graphite substrate have been investigated using electrodes after preliminary intercalation and without this stage and involving methods of the cyclic voltammetry, electronic microscopy and general principles of the irreversible thermodynamics. Potentials of the intercalation and deintercalation starting points, potentials of the anodic and cathodic maximums have been determined and changes in the free Gibbs energy for the intercalation and deintercalation processes, changes in the enthalpy and enthropy of these processes, diffusion and migration fluxes of the hydrosulfate ions were calculated using the experimental data. Criteria of Schtakelberg, Tomesh and Shevchik and measurements of an amount of electricity required for the processes were used to evaluate the reversibility ratio of intercalation and deintercalation. It was found that raise in the intercalation-deintercalation cycles number results in increase in the limit anodic current value. This increase may be caused by partial decomposition of the graphite substrate structure and faster intercalation of the hydrosulfate ions during next cycles. Evaluation of the diffusion and migration fluxes of hydrosulfate ions has been made using an electronic microscopy. Thermodynamic moving forces of the fluxes have been analyzed. The higher is the concentration of sulfuric acid, the higher is the surface concentration of sulfur. A value of the flux of the electrochemical intercalation of hydrosulfate ions from a 1 M solution of sulfuric acid is about 42 times higher comparing to the physical intercalation flux value. A contribution of the latter flux into the total intercalation flux is only 3.8 % from the electrochemical intercalation flux contribution.*

Keywords: intercalation; sulfuric acid; electrochemical; parameters; diffusion; ions migration

Introduction

Graphite is a material with numerous applicable physico-chemical properties, which can be used in various production branches. Atoms and molecules of various substances can be embedded into graphite and change its properties.

Graphite can interact with many acids: nitric, hydrofluoric, phosphoric, trifluoracetic and chloric if a strong oxidizing agent is present. Graphite hydrosulphate was synthesized by P. Schaufheitel and became the first known chemical compound of graphite [1]. Now this compound is used in technologies of the graphite sealers production [2]. Some graphite modification products can be used as a source or raw material in various technological processes. For example, this material is used as a source for production of thermally expanded graphite. Graphite can be modified with chemical, physical and electrochemical methods.

Intercalated graphite usually reveals increased electroconductivity. For example, conductivity of the intercalated $C_{24}Cl$ is higher than conductivity of gold. Intercalated carbon nanomaterials can be used as electrodes in the processes of electrochemical production of hydrogen.

Intercalated graphite products are widely used in various applications such as lithium-ion batteries (as an electrode material), synthetic conductors, catalysts for some petrochemical processes, lubricants (especially for use in chemically aggressive media), membranes, fire-protection coverings, etc [4].

Thermotreatment of the intercalated graphite products results in destruction of the embedded sulphuric acid, which causes significant (300-500 times) expansion of the crystallites and formation of flexible and tortuous particles of the thermo-expanded graphite [1]. All useful characteristics of the regular graphite are retained in this product, which also has higher surface area can be treated mechanically (pressed, rolled) without any additional adhesion agent [5-7]. Plain (non-reinforced) thermo-expanded graphite materials can endure heating up to 500-550 ^{0}C in the air [8, 9], up to 650 ^{0}C in the steam and 3000 ^{0}C in the inert medium and stay mechanically durable at freezing to -240 ^{0}C [10]. This material is chemically inert and retains high electro- and thermoconductivity [8].

The thermo-expanded graphite can be used as adsorbent for collection of the spilled oil products [11, 12] and as source material for manufacturing of membranes and filters [13].

Thermo-expanded carbon can adsorb inorganic compounds same as organics. For example, it can be used for adsorption of gold and copper ions [14].

An American company Union Carbide has patented a special foil of the thermo-expanded graphite, which can be used as a sealer. Graphite sealers and stuffing blocks are very durable, they wear-resisting and inert in many chemically aggressive media [4]. Some products of the graphite intercalation can be used as a fireproof expandable dye-coating for the electric cables. In the case of fire or excessive heating it expands and forms a strong shell preventing further burning. This coating protects the substrate against heating up to 500 ^{0}C and can be applied to some metal constructions [1].

An electrochemical method of intercalation and synthesis of the embedded products (EP) is more favourable than pure chemical modification. The first method is more ecologically safe; it requires low concentrated acids and can be realized in a well-controlled regime, which ensures production of EP with predefined composition and purity. The electrochemical intercalation primary requires such acids: H_2SO_4, HNO_3, $HClO_4$, H_2SeO_4, CF_3COOH, $HCOOH$. Most experimental results of the carbon materials oxidizing relate to the compact and well-structured materials. Some results related to the kinetics and mechanism of anodic processes occurring on the dispersed graphite electrodes in 15-60 % solutions of HNO_3 are also available [15]. It was found that thermo-expandable graphite compounds can be synthesized only within some region of the anode potentials.

Therefore, investigation of synthesis and possible applications of the intercalated graphite products seems very topical and interesting however, information related to specific details of intercalation and deintercalation of hydrosulphate ions is insufficient.

Our work was aimed onto investigation of the above mentioned processes and analysis of properties of the hydrosulphate-embedded carbon materials.

Experimental

The hydrosulphate ions intercalation into the graphite substrate has been investigated for the aqueous solution of sulphuric acid in the range 1-15 m/l. The results of the intercalation were analyzed using a cyclic voltammetry (CVA) and electron microscopy.

The following graphite samples were used as source materials for electrodes: 1)crucible graphite (referred hereafter as GE-1 electrode); 2)BSP-20AS/High brand graphite made by the Japanese company "Chuetsu Graphite Works Co. Ltd." (GE-2 electrode). A suspension containing 90 % of the source graphite and 10 % of the adhesive (polyvinylidenchloride in 2-methylpyroliden) has been prepared and then the graphite composition was deposited on the platinum substrate. A silver chloride electrode in the saturated solution of KCl and mercury sulphate electrode in the 1 M solution of H_2SO_4 were used as reference electrodes. All experiments were carried out using a standard electrode cell YaSE-2.

Anodic polarization was ranged from 0 to 1200 mV. Upper limit of the polarization was set according to previous investigation of the working electrolytes decomposition potentials on the graphite electrodes. Cathodic part of the CVA curve was inversed to the anodic and ranged from +1200 to 0 mV. Temperatures of the working solutions were from 293 to 323 K and the CVA potential change speeds were 0,005-0,100 V/s (for the anodic part) and 0,02-0,10 V/s (for the cathodic part).

The potentials of the intercalation and deintercalation starting points ($\varphi_{start(A)}$ and $\varphi_{start(C)}$) and potentials of the highest cathodic and anodic currents ($\varphi_{max(A)}$ and $\varphi_{max(C)}$) were determined using CVA (see Fig. 1). These parameters made possible to calculate changes in the Gibbs free energy for the intercalation ($\Delta G_{start(A)}$) and deintercalation ($\Delta G_{start(C)}$) starting points, changes for the points of the highest speed of intercalation ($\Delta G_{max(A)}$) and deintercalation ($\Delta G_{max(C)}$) and enthalpy (ΔH) and entropy (ΔS) changes for these processes. Indexes A and C mean anodic process (intercalation) or cathodic process (deintercalation) respectively.

The concentrations of carbon, sulphur and oxygen in the surface layer of the modified graphite materials were found and fluxes of the physical and electrochemical transport of hydrosulphate ions towards the carbon matrix were calculated.

Results and discussion

An electrochemical system for the hydrosulphate intercalation/deintercalation has been designed according to the following scheme:

$$\text{Me} \mid \text{C}\,(HSO_4^-) \mid H_2SO_4,\ H_2O \,\dagger\dagger\, H_2O,\ \text{KCl},\ \text{AgCl} \mid \text{Ag} \mid \text{Me} \qquad (1)$$

The thermodynamic parameters of the systems were calculated using relations – $\Delta G = n \cdot F \cdot E$, $\Delta S = -(\partial \Delta G/\partial T)_p$, $\Delta H = \Delta G + T \cdot \Delta S$, where ΔG is Gibbs free energy change, n – quantity of electrons acting in the elementary electrochemical stage, F – Faraday's constant, E – e.m.f, ΔS – change of entropy, T – temperature and ΔH – change of enthalpy for the resulting electrochemical process [16].

Carbon electrodes with preliminary intercalated hydrosulphate ions were used to determine thermodynamic parameters of the circuit (1). An inter-phase potential C (HSO_4^-) | H_2SO_4, H_2O was considered equilibrium.

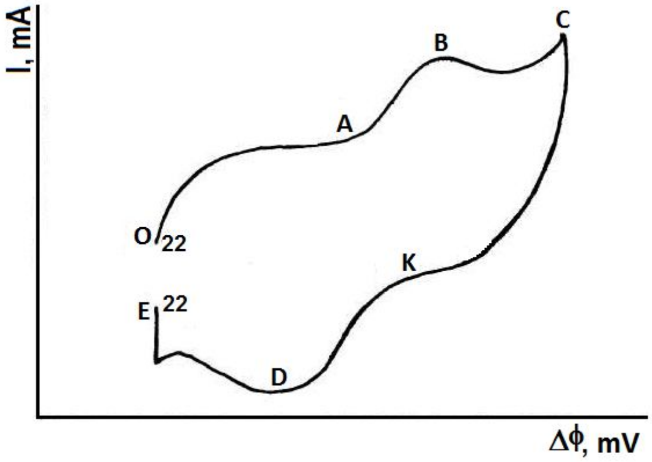

Figure 1. A typical CVA curve for intercalation/deintercalation processes for electrodes GE-1, hydrosulphate ions, potential change speed $2 \cdot 10^{-2}$ V/s, 3 M solution of sulphuric acid and mercury sulphate reference electrode.

A Schtakelberg's method has been employed to assess a reversibility ratio of the intercalation/deintercalation processes. A tilt angle of a tangent to the CVA curve in the point $\varphi_{1/2}$ can be calculated using this method through the relation:

$$\left(\frac{d\bar{I}}{d\varphi}\right)_{\varphi_{1/2}} = -\frac{n}{A}\bar{I}_d,$$

where n means quantity of electrons participating in the intercalation.

A value of the parameter "A" from relation above should be equal to 100.7 mV for the single-electron process at 293 K. An experimental value of "A" for the system with GE-2 electrode and concentration of sulphuric acid 3 m/l was ≈ 101 mV.

The criterion of Tomesh states that a difference between $\varphi_{3/4}$ i $\varphi_{1/4}$ for the reversible voltammetry curves recorded at 298 K should be 56 mV [17]. In our case this difference was 60 mV.

A difference between the cathodic and anodic peak potentials for a reversible process occurring at the solid electrodes should be equal to the theoretical value calculated through the Shevchik relation [17] $\Delta\varphi_{rv} = \varphi_a - \varphi_c = 2{,}22(RT/nF)$, where φ_a and φ_c denote peak potentials for the anodic and cathodic parts of the CVA curve. A theoretical value of $\Delta\varphi_{rv}$ should be 80.7 mV at 293 K. Our experimental results gave $\Delta\varphi_{rv}$ = 70 mV.

A quantity of electricity spent for the intercalation/deintercalation processes (Q) has been determined in order to evaluate their reversibility [18]. Since $Q_{int}=0{,}9\ Q_{deint}$ for both GE-1 and GE-2 electrodes these processes can be considered as reversible.

Preliminary experiments with non-intercalated electrodes proved that previous intercalation/deintercalation cycles can influence parameters of next intercalations (see Fig. 2). For example, previous cycles result in higher value of the limit anodic current, which can be caused by defects in the graphite substrate remained after previous embeddings. New anions can faster embed into defective spots of the substrate during next intercalations.

Higher speed of the potential change results in small positive shifting of $\varphi_{max(A)}$.

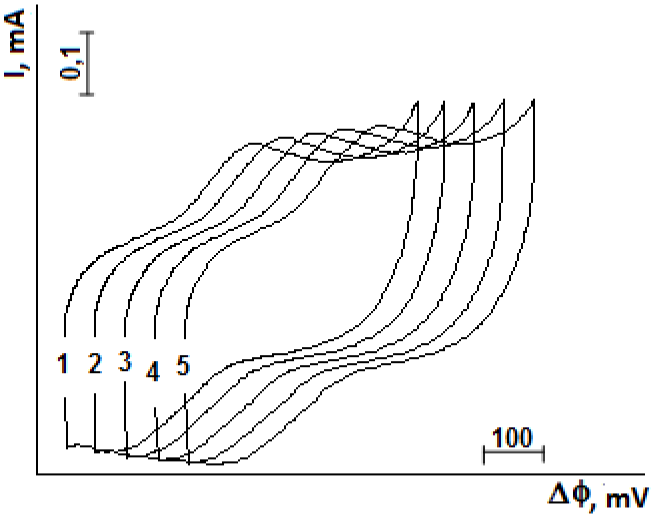

Figure 2. Consecutive CVA curves for intercalation/deintercalation processes on GE-1 electrode and 1 M solution of sulphuric acid with silver chloride reference electrode.

Absolute values of the intercalation enthalpy change for the electrode GE-2, which underwent preliminary intercalation (under the following conditions: C(H_2SO_4) = 3 m/l, mercury sulphate reference electrode, intercalation current i_{int} = 35 mA/sm^2, intercalation time 10 min) and decrease at the raise of temperature according to the formula: $\Delta H_{int} = -0,0434 \cdot T + 52,873$.

Deintercalation of the same electrode under similar conditions gives the following relation for the enthalpy changes: $\Delta H_{deint} = 0.4394 \cdot T + 0,147$.

Previous intercalation causes decrease in the intercalation potential φ_{int} at next intercalation and in absolute changes in the free Gibbs energy of the intercalation ΔG_{int}. An absolute value of the intercalation enthalpy $|-\Delta H_{int}|$ raises.

Intercalation of graphite in the aqueous solutions has been extensively investigated by many authors but results of different works are quite controversial [19-22]. Authors of [21] reported better intercalation results that can be achieved in the concentrated solutions while no intercalation occurred for a 10 % solution of sulphuric acid. On the other hand, successful intercalation of graphite in the 0.1 M solutions of H_2SO_4 has been reported in [22]. This concentration corresponds to a quite diluted 0.98 wt % solution. A completely reversible intercalation in the 4 M (~ 31.8 wt %) solution of sulphuric acid has been reported in the same reference. Good agreement was achieved only for the results [19-22] related to the highly concentrated systems containing 60 wt % of the acid or more. No data of composition of the graphite intercalation products in the diluted solutions are available.

Two maximums can be found on the CVA curves recorded for the diluted solutions. One of them appears on the anodic and another one – on the cathodic (see Fig. 1). Two maximums in the anodic part and another two in the cathodic have been recorded during intercalation in the 10 M solution of H_2SO_4 (see Fig. 3).

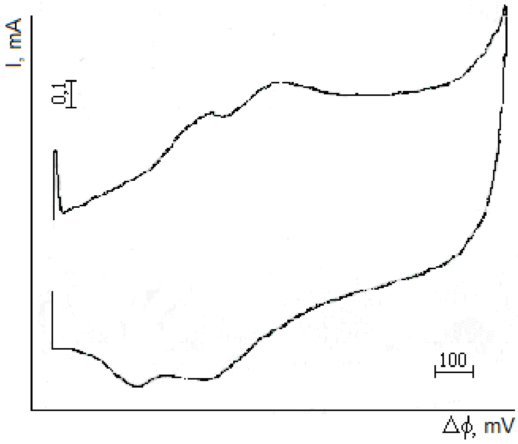

Figure 3. CVA curve for the 10 M solution of H_2SO_4.

A method of the polarization diagrams in the aqueous solutions of H_2SO_4 [23] has been employed to investigate destruction of the graphite electrodes. Following processes can occur at the graphite destruction:

$$\mathbf{C_x^+HSO_4^-} + H_2O \rightarrow \left[(\mathbf{C_x^+O})^- \mathbf{H^+}\right] + \mathbf{H_2SO_4} \quad (2)$$

$$(\mathbf{C_x^+(HSO_4^-)(2H_2SO_4)})_n \rightarrow (\mathbf{C_x^+(2HSO_4^-)(H_2SO_4)})_n^- + H^+ \quad (3)$$

An intercalation current density consists of two components: diffusive current and the current, which depends on the particles transportation at formation of the oxide compounds. Process (3) causes decrease in the electric resistance because of transformation of the graphite-embedded H_2SO_4 molecule into an electroactive ion HSO_4^- [20]. The maximal corrosion current determined in our experiments was found insignificant comparing with the total intercalation current. This proves that the process of intercalation can run in the diluted solutions of sulphuric acid.

A change in the decomposition energy $\Delta U = - n \cdot F \cdot \Delta\varphi$ of the graphite intercalation compounds (GIC) for various concentrations of the acid has been calculated in order to evaluate thermodynamic possibility of the decomposition. Current consumption for the side processes decreases with decrease of the acid concentration for $C(H_2SO_4)$ = 10-15 M. This result is in a good agreement with the reference [24]. The maximal corrosion current has been recorded for the 10 M solution.

A contribution of the corrosion current into the total process current value remains insignificant even in the diluted solutions.

CVA and the electron microscopy with EDX – Shimadzu 900 HS, ICP MS Agilent – SUA were engaged to determine surface content of sulphur and oxygen after the 30 min long amperostatic intercalation with current density 40 mA/sm^2. Working area of the electrode was 0.25 sm^2.

The spectral characteristics of the GE-1 surface before intercalation are represented in Fig. 4 and Table 1. Fig. 5 and Table 2 represent results related to the same sample after intercalation.

Table 1

Spectral investigation of the surface composition of a graphite sample before intercalation

El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	Error [%]
C	6	K-series	99.47	99.48	99.81	0.3
S	16	K-series	0.45	0.45	0.17	0.0

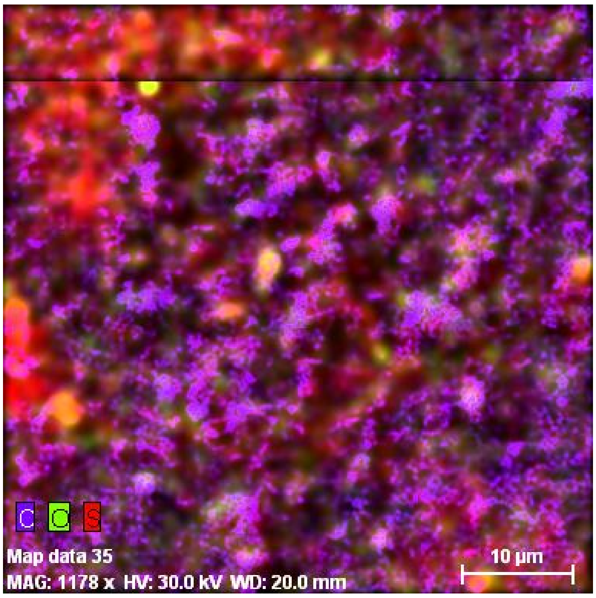

Figure 4. Surface map of a graphite sample before intercalation.

Table 2
Spectral investigation of the surface composition of a graphite sample after intercalation in the 5 M solution of H_2SO_4.

El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	Error [%]
C	6	K-series	26.08	26.08	33.35	8.3
O	8	K-series	65.57	65.58	62.95	20.9
S	16	K-series	7.63	7.63	3.66	0.3

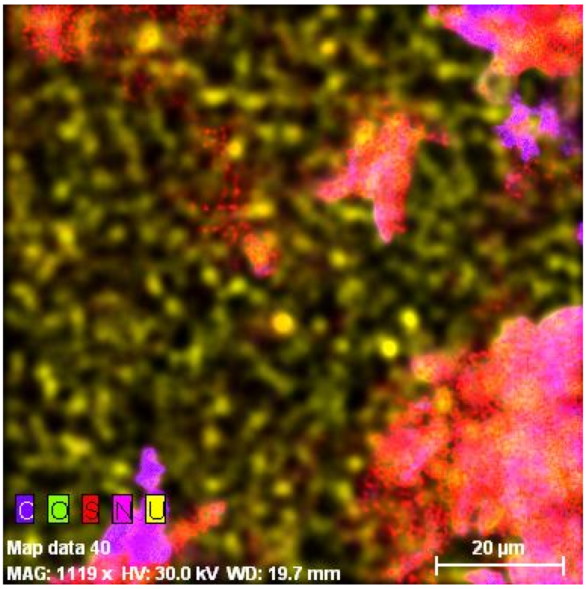

Figure 5. Surface map of a graphite sample after intercalation in the 5 M solution of H_2SO_4.

Surface atomic concentrations of carbon, sulphur and oxygen are shown in Fig. 6.

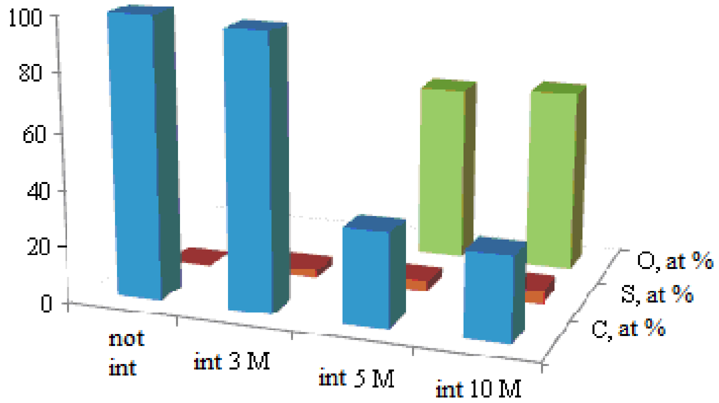

Figure 6. Dependence of the surface concentrations of carbon, sulfur and oxygen on concentration of sulfuric acid during electrochemical intercalation.

The interface gradients of chemical and electric potentials should exist on the boundary graphite surface | sulphuric acid solution in order to ensure embedding of hydrosulphate ions into the graphite matrix. Only physical intercalation can run if a gradient of the hydrosulphate ions chemical potential is the only gradient existing in the system. Carbonium cations can be formed in the system if electric potential also exists and these cations facilitate faster intercalation of hydrosulphate anions into the matrix. An aggregated effect of both gradients can be characterized through the difference in the electrochemical potentials of hydrosulphate ion ($\Delta\tilde{\mu}_i$) on the interphase boundary graphite | solution of sulphuric acid:

$$\Delta\tilde{\mu}_i = \Delta\mu_i + \Delta\psi ,$$

where $\Delta\mu_i$ and $\Delta\psi$ mean interphase differences in the chemical and electric potentials of the ions respectively.

Physical intercalation has been carried out using solutions of sulphuric acid with concentrations 1.0; 3.0; 5.0; 10.0 and 15.0 M during 60 min.

Electrochemical intercalation has been carried out using similar solutions with intercalation current 10 mA and samples area 0.25 sm^2 during 30 min.

Table 3

Hydrosulphate ions intercalation conditions. № - graphite sample number, C(H_2SO_4) – concentration of sulphuric acid, t – intercalation time, I_{int} – intercalation current. Contents of elements in wt. % denoted as C(X), where X means carbon C(C), sulphur C(S) and oxygen C(O). Relative error of determination (%) is shown in the square brackets

№	Type of intercalation	C(H_2SO_4) mol/l	t, min	I_{int}, mA	C(C)	C(S)	C(O)	C(O)/C(S)
5	electrochemical	1.0	30	10	27.85 [9.6]	4.77 [0.2]	65.92 [21.8]	13,8
6	electrochemical	10.0	30	10	17.22 [6.3]	9.61 [0.4]	70.80 [23.0]	7.4
7	electrochemical	15.0	30	10	94.86 [1.3]			
8	Physical	1.0	60	–	20.50 [6.3]	0.22 [0.0]	61.43 [20.7]	279.2
9	Physical	3.0	60	–	25.11 [7.7]	0.30 [0.0]	58.26 [20.2]	194.2
10	Physical	5.0	60	–	22.72 [7.0]	0.52 [0.0]	63.02 [21.0]	121.2
11	Physical	10.0	60	–	25.33 [7.8]	0.73 [0.1]	58.59 [20.4]	80.3
12	Physical	15.0	60	–	24.38 [7.6]	1.55 [0.1]	62.15 [21.0]	40.1

The spectral parameters have been recorded for small selected parts of the electrode surface only. Nevertheless, even these results prove that higher concentration of sulphuric acid during physical intercalation results in higher surface concentration of sulphur on the electrode (see Fig. 7).

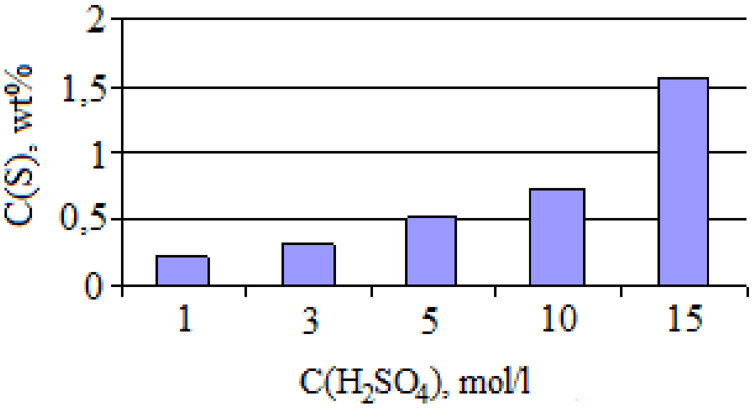

Figure 7. Influence of concentration of sulphuric acid ($C(H_2SO_4)$, m/l) on the surface content of sulphur (C(s), wt %) after physical intercalation.

Increased concentration of H_2SO_4 during electrochemical intercalation also results in higher surface content of sulphur (Fig. 8).

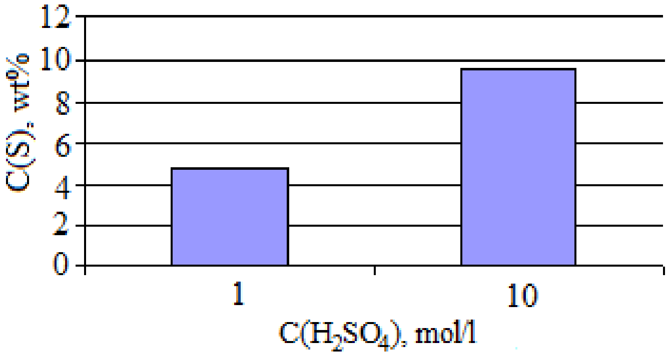

Figure 8. ***Same as Figure 7 but for*** **the electrochemical intercalation.**

Relatively high surface content of oxygen can be caused by formation of the carbon oxide compounds in the surface layer of graphite as a result of reaction between embedded hydrosulphate ion and water molecule:

$$C_x^+HSO_4^- + H_2O \rightarrow \left[(C_x^+O)^- H^+\right] + H_2SO_4 \quad (4)$$

The raise in concentration of H_2SO_4 from 1.0 to 15.0 m/l agrees with the increase in the surface content of sulphur and decrease of the ratio C(O)/C(S). This can be caused by retardation in the reactions (4) rate with increasing of concentration of sulphur acid. The fluxes of the electrochemical and physical intercalation have been evaluated basing on the spectral investigation of the electrodes surface. The evaluation has been made through determination of a mass of the embedded sulphur after a 30 min process on the 0.25 sm^2 electrode area and with intercalation current 10 mA. The evaluation results are represented in Table 4 and Fig. 9.

Table 4

Fluxes of the hydrosulphate ions intercalation into the graphite matrix. J means total flux of the ions and J' – the specific flux on a unit surface area per unit of time (g/min sm^2)

Intercalation conditions	Sample	Time, min	C(S), g	C(S), for 30 min	J'	J
1 M sulphuric acid						
Electrochem	5	30	4.77	4.77	4.77	0.636
Physical	8	60	0.22	0.11	0.11	0.015
10 M sulphuric acid						
Electrochem	6	30	9.61	9.61	9.61	1.28
Physical	11	60	0.73	0.365	0.365	0.049

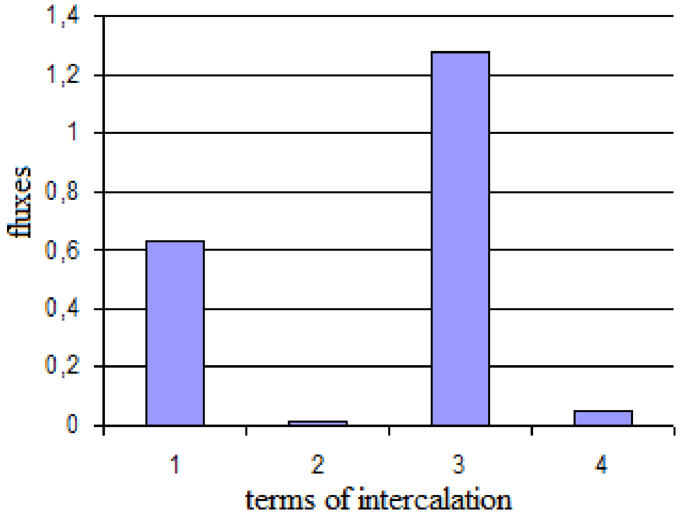

Figure 9. Electrochemical (1 and 3) and physical (2 and 4) fluxes (g/min·sm^2) of the hydrosulphate ions intercalation for the 1 M (1 and 2) and 10 M (3 and 4) sulphuric acid.

An electrochemical intercalation flux value was 0.636 g/min·sm^2 and a physical flux value was 0.015 g/min·sm^2 for the 1 M sulphuric acid. Corresponding fluxes for the 10 M solution were 1.28 and 0.049 g/min·sm^2.

Conclusion

The processes of intercalation and deintercalation, which run under the above mentioned experimental conditions, can be classified as reversible. A contribution of the current caused by the corrosive destruction of the graphite matrix is insignificant.

As concentration of sulphuric acid is increasing from 1.0 to 10.0 m/l, the physical intercalation flux raises from 0.015 to 0.049 g/min·sm^2 and the electrochemical raises from 0.636 to 1.28 g/min·sm^2. This change in H_2SO_4 concentration also causes raise in the "physical intercalation" bringing contribution to the total flux of anions from 2.3 to 3.8 %.

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