

SORPTION PROPERTIES OF EXFOLIATED GRAPHITE DOPED WITH IRON COMPOUNDS

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Introduction

In a modern industry functional carbon materials are known to take on special significance. Among them the particular place is occupied by the exfoliated graphite – a lightweight carbon material possessing several properties: various heat- and electro-conductivities, the developed pore structure and the ability to be compacted with no binder to give carbon articles with variable densities and gas permeabilities [1].

Exfoliated graphite has developed porous structure due to the presence of micropores, mesopores and macropores. Specific surface of exfoliated graphite determined by low-temperature adsorption of nitrogen is in the range of 30 - 150 m²/g. The high-porosity makes it possible to use exfoliated graphite for the sorption of hydrocarbons, such as for recycling oil spill [2].

Besides, nowadays there are still some problems preventing uses exfoliated graphite as an absorbent. The main problem is to spray it onto the place of pollution and to gather exfoliated graphite after sorption. That is why the aim of our research work was to obtain exfoliated graphite doped with iron compounds, possessing magnetic properties, and to study several its properties [3].

Experimental

At the first step of our preparation we obtained expandable graphite by anodic polarization of the natural graphite. This process was carried out in a three-electrode cell with the iron containing electrolyte. Graphite was used as anode. The potential was measured relative to the standard Ag/AgCl reference electrode. Electrolyte for syntheses was saturated solution of Fe(NO₃)₃ (ω(Fe)=11%, ω(NO₃)=36%); Graphite was oxidized under galvanostatic mode - passing a quantity of electricity per unit weight: Q = 500 - 1500 A*s/g. The used stabilized current was equal to 30 mA [4].

After synthesis, the electrolyte excess was removed and the samples were dried at 60 °C for 2 h. Exfoliated graphite was produced by expandable graphite flash-heating up to 250, 400 and 900 °C.

Phase composition of the samples was controlled by X-ray diffraction analysis. The specific surface area and pore structure of exfoliated graphite was determined by nitrogen adsorption measurements on QSurf-series device. Images of scanning electron microscopy and energy dispersive X-ray spectroscopy of the exfoliated graphites surfaces were performed with a scanning electron microscope Jeol JEM-5510 with an attachment for X-ray microanalysis of INCA. Thermogravimetry (TG) and differential scanning calorimetry

(DSC) was performed on synchronous termoanalyzer NETZSCH STA 449C Jupiter over the temperature range of 30-500 °C in nitrogen flow. ⁵⁷Fe Mossbauer spectra (MS) were acquired in transmission geometry using a ⁵⁷Co/Rh source mounted on a standard constant acceleration spectrometer. The magnetic measurements were carried out using Faraday balance at room temperature. The sorption ability of exfoliated graphite was studied for samples, compacted to the density of 0,03 g/cm³ in relation on octane (viscosity η = 0,5 mPa*s) and motor oil (η = 83,5 mPa*s).

Results and Discussion

The results of the anodic polarization of natural graphite are presented at the table 1. XRD showed, that in expandable graphite reflections corresponding to the graphite phase (G) and graphite oxide (GO) are observed. The iron content in the samples does not depend on the passing quantity of electricity per unit weight and is about 7 mass.%.

Table 1. The Characteristics of Expandable Graphite.

Sample	Passing quantity of electricity per unit weight, A*s/g	Phase composition (d _i , Å)	ω (Fe), %
EG-1	500	G (3,35 Å)	7,2
EG-2	800	G (3,35 Å)	7,4
EG-3	1000	G (3,35 Å), GO	7,2
EG-4	1200	G (3,35 Å), GO	7,1
EG-5	1500	G (3,35 Å), GO	7,4

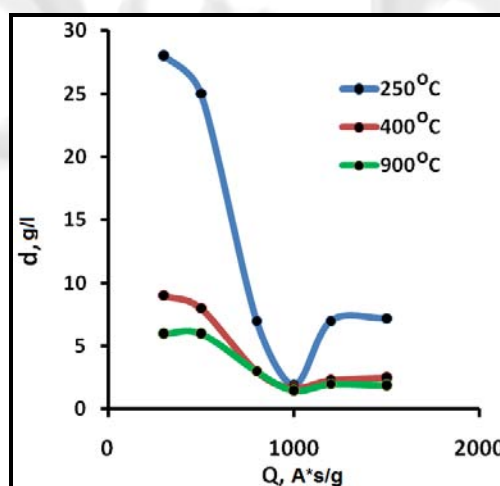


Fig. 1 Dependence of the exfoliated graphite bulk density on the passing quantity of electricity through natural graphite.

After preparation expandable graphite was subjected to the thermal shock at the temperature 250 – 900 °C. The main characteristic of exfoliated graphite is a bulk density – $d_{EG} = m_{EG}/V_{EG}$. The lower bulk densities, the higher the sorption activity of exfoliated graphite. Dependence of the exfoliated graphite bulk density of the passing quantity of electricity through natural graphite at different temperatures shock is presented in fig.1. Industrial exfoliated graphite have bulk

density of 8 g/l at 600 °C and 3 g/l at 900 °C [1]. Several our exfoliated graphite possess bulk density of 1 – 3 g/l already at 250 °C. This phenomena is due to the presence of graphite oxide in the expandable graphite, that proved with XRD and thermal analyses.

According to XRD, the phase composition of exfoliated graphite, obtained at the 250 – 400 °C, is presented only by graphite phase, but the one for sample obtained at the 900 °C is presented by graphite and α -Fe₂O₃ phases.

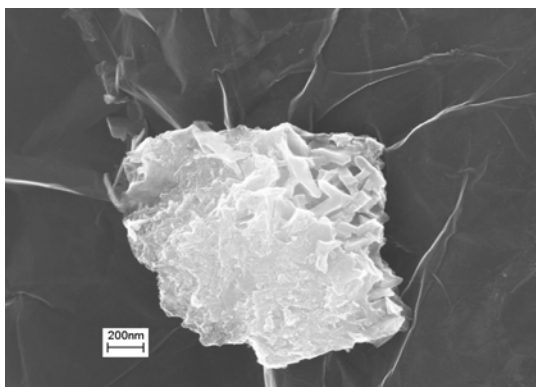


Fig. 2 SEM image of exfoliated graphite doped with iron oxides.

According to scanning electron microscopy (SEM) and Energy dispersive X-rays (EDX) analysis data, iron (III) oxides particles with size of 7 – 3000 nm are distributed over the entire exfoliated graphite (fig. 2).

Mossbauer spectroscopy showed, that exfoliated graphite, obtained at any temperature, consist of mixture of α -Fe₂O₃ and γ -Fe₂O₃ at the magnetic and superparamagnetic states due to the different particle sizes. Exfoliated graphite obtained at 400 °C from EG-3 contains 13 % γ -Fe₂O₃ at the ferromagnetic state, 27 % γ -Fe₂O₃ at the superparamagnetic state and 60 % α -Fe₂O₃ at the superparamagnetic state at room temperature. But in the exfoliated graphite, obtained at 900 °C, content of γ -Fe₂O₃ at the ferromagnetic state increases up to 22 %.

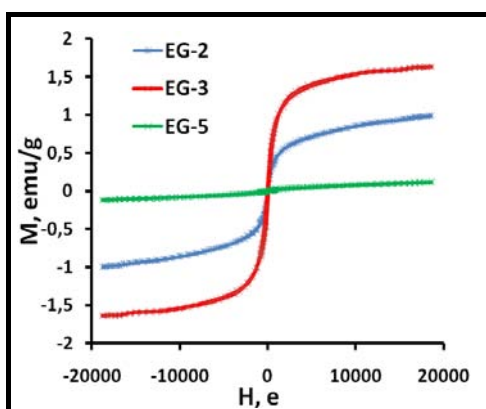


Fig. 3 Results of the magnetic measurements of exfoliated graphites.

Magnetic measurements of exfoliated graphite confirmed that we have obtained the materials with magnetic properties. Fig. 3 shows the curves of the magnetization of different types of exfoliated graphite on the strength of the magnetic field.

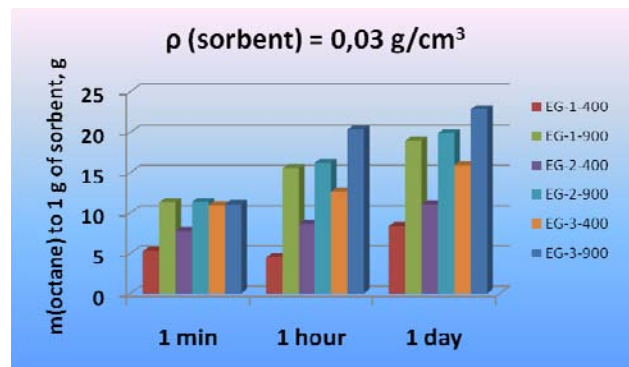


Fig. 4 Sorption activity of the exfoliated graphite to the octane.

Results of the study of exfoliated graphites sorption properties are presented in the fig.4. As shown, obtained materials possess with high sorption capacity, which reaches value of 23 g of octane per unit weight of the sorbent. The sorption of motor oil flows similar, but sorption activity lower for 30 % due to an increase in viscosity of the adsorbed substance.

Conclusions

Thus, in our preparations we obtained exfoliated graphite possessing with both high sorption capacity and magnetic properties. Sorption capacity reaches a value over 20 g of octane and over 15 g of motor oil per unit weight for exfoliated graphite, compacted to the density of 0,03 g/cm³. Magnetic properties the materials are due to γ -Fe₂O₃, which together with α -Fe₂O₃ is distributed over the exfoliated graphites surfaces.

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References

- [1] Sorokina N.E., Redchitz A.V., Ionov S.G., Avdeev V.V. Different exfoliated graphite as a base of sealing materials. *J. of Phys. Chem. Sol.* 2006; 67: 1202-1204.
- [2] Toyoda M., Inagaki M. Heavy oil sorption using exfoliated graphite. *New application of exfoliated graphite to protect heavy oil pollution. Carbon* 1999; №38. P.199-210.
- [3] Fan N., Ma X., Ju Z., Li J. Formation, characterization and magnetic properties of carbon-encapsulated iron carbide nanoparticles. *Materials Research Bulletin* 2008; 43: 1549-1554.
- [4] Shornikova O.N., Sorokina N.E., Avdeev V.V. The effect of graphite nature on the properties of exfoliated graphite doped with nickel oxide. *J. of Phys. and Chem. of solids* 2008; 69: 1168-1170.