

## PORE STRUCTURE OF EXFOLIATED GRAPHITE

*O.N. Shornikova, E.V. Kogan, D.V. Petrov, N.V. Maksimova,  
N.E. Sorokina*

Lomonosov Moscow State University, Leninskie gory, 1,  
building 3, Moscow 119991, Russia

### Introduction

Exfoliated graphite (EG<sup>T</sup>) is a light-weight carbon material remaining all the graphite properties supplemented with a developed pore structure and an ability to be compacted in goods without a binder. EG<sup>T</sup> pore structure is represented by micro-, meso- and macro-pores providing already existing and promising applications of such material [1-4]. The exfoliated graphite ability for compacting into foils is due to the presence of macropores [3]. Combination of micro- and meso-pores makes exfoliated graphite a perspective hydrocarbons adsorbent and a gas-storage container [1-2]. Developed pore structure coupled with the compacting ability makes EG<sup>T</sup> a promising catalyst support [4].

Numerous researches revealed the correlation between EG<sup>T</sup> and its-based materials properties (bulk density, sorption capability, strength and elasticity) and the way of exfoliated graphite preparation [1-4]. Nevertheless, pore structure of exfoliated graphite was investigated mostly for industrial samples or EG<sup>T</sup> prepared through graphite bisulfate [3]. Herein we report study of pore structure of exfoliated graphite prepared through chemical or electrochemical route using nitric acid or metal nitrates.

### Experimental

Natural graphite flakes (G) with an average diameter of 300-400 μm, 98% nitric acid, reagent-grade Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and distilled water were used as parent substances. Expandable graphite (EG) samples were prepared as follows. EG-1 was synthesized by successive treatment of graphite with 98% HNO<sub>3</sub> for 30 min at a constant stirring and hydrolysis. EG-2 was prepared through graphite anodic polarization in 60% HNO<sub>3</sub> followed by hydrolysis. EG-3 was obtained as a result of graphite intercalation with 98% HNO<sub>3</sub> followed by anodic oxidation in 60% HNO<sub>3</sub> and hydrolysis. EG-4 was prepared by graphite anodic polarization in saturated solutions of nickel nitrate. Graphite anodic polarization was carried out in the three electrode cell where graphite compressed with a constant pressure was used as an anode, platinum disk was a current supplier, platinum plate of the same area was a cathode and Ag/AgCl electrode was used as a reference electrode. 60% aqueous solution of nitric acid and saturated aqueous solutions of nickel nitrate were used as electrolytes. The polarization was carried out at a stabilized constant current of 100 and 30 mA for nitric acid and Ni(NO<sub>3</sub>)<sub>2</sub> solutions correspondingly. The specific charge passed through graphite was of 1500 C/g. Hydrolysis lays in samples water treatment in a weight ratio G:H<sub>2</sub>O of 1:20. Sample EG-4 was not subjected to hydrolysis. All expandable

graphite samples were dried in air at a temperature of 30°C for 24 hours.

Momentary thermal treatment of expandable graphite at temperature of 250 and 900°C in air gives exfoliated graphite. Samples were analyzed by X-ray diffraction and Raman spectroscopy. Specific surface area, pore volume and distribution were determined by low-temperature nitrogen adsorption on a Sorptomatic 1900 device in a p/p<sub>s</sub> range from 0 to 1.

### Results and Discussion

According to XRD data, phase composition of EG-1 is represented by graphite with an interlayer distance of 3.36 Å and graphite nitrate of VIII stage. XRD patterns of all the other EG samples besides the graphite peaks contain a halo in 2θ range of 5-15° related to graphite oxide appearing as a result of graphite oxidation by oxygen evolved during water decomposition occurred at reaction potentials.

EG-2, EG-3 and EG-4 are able to expand as low as 250°C giving exfoliated graphite with a bulk density of 1.5-2.0 g/l whereas EG-1 almost does not expand under such a condition (Table 1). This fact is due to an exothermal decomposition of graphite oxide providing the additional heat that is enough for the whole sample warming up and exfoliation. Increasing of exfoliation temperature leads to EG-1 bulk density reduction meaning that the imparted heat is getting enough for evaporation intercalated substance and sample expansion.

**Table 1. Bulk densities of exfoliated graphite samples.**

Sample	Bulk density, g/l			
	EG <sup>T</sup> -1	EG <sup>T</sup> -2	EG <sup>T</sup> -3	EG <sup>T</sup> -4
250°C	74	2.0	1.7	1.5
900°C	2.2	1.1	1.3	3.0

The shape of nitrogen adsorption isotherms allows assuming that exfoliated graphite possess developed pore structure and is mostly meso-porous material (fig.1). There are several extremes on the differential pore size distribution curve referred to pores with different diameters (fig.2). The smallest pores radius is of 1.5-2.2 nm, the next pore radius is about 5 nm and the largest pores that is possible to discover with nitrogen adsorption has a radius of 8 nm. The pore radiuses are almost the same for all the samples that is probably due to the peculiarity of graphite structure. The slight difference was noted for the sample EG<sup>T</sup>-4 with an average pore radius of 1.5 nm that is probably because of partial pore capping with NiO particles containing in this sample.

Specific surface area of the samples varies from 30 to 220 m<sup>2</sup>/g and pore volume is about 0.15-0.52 ml/g (Table 2). It is interesting to note that EG<sup>T</sup>-3 and EG<sup>T</sup>-4 obtained at 250 °C possess the larger surface area than samples prepared at 900°C. Moreover, their pore volume is also of a greater value.

Structural investigations were carried out in order to explain such a behavior.

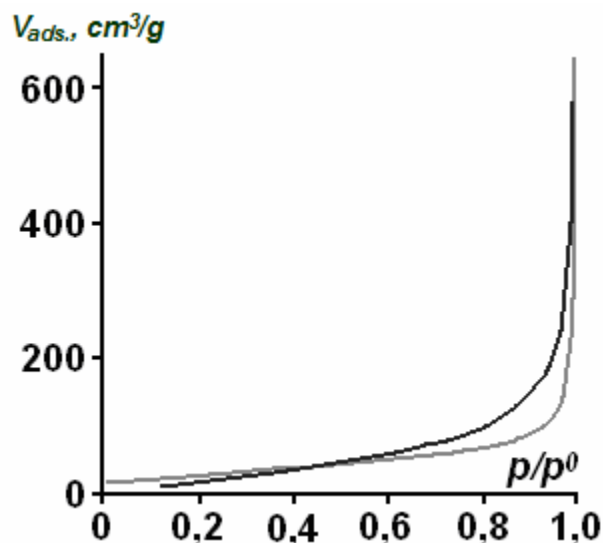


Fig. 1 The nitrogen adsorption isotherm for the EG<sup>900</sup>-2 sample.

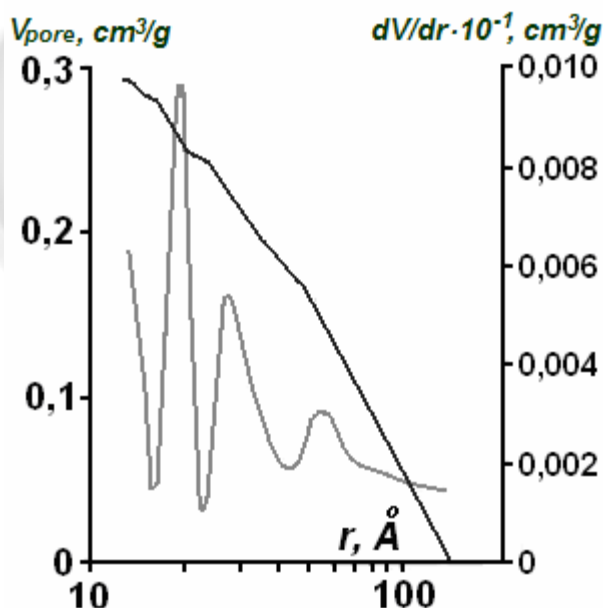


Fig. 2 The differential pore size distribution curve for the EG<sup>900</sup>-2 sample.

According to XRD data, graphite electrochemical oxidation causes significant reduction of graphite crystalline size along c-axis (Table 2). Thus the more quantity of intercalated species are located in the intercrystalline areas providing the more complete particle expansion during thermal treatment that could partly explain the surface area incensement.

Table 2. Specific surface area and pore volume of exfoliated graphite samples.

Sample	EG <sup>T</sup> -1	EG <sup>T</sup> -2	EG <sup>T</sup> -3	EG <sup>T</sup> -4
$S_{BET}, m^2/g$				
250°C	5	60	220	140
900°C	45	150	100	30
$V, ml/g$				
250°C	0	0.21	0.52	0.38
900°C	0.17	0.34	0.27	0.15
Crystalline size $L_c, nm$				
	60	15	10	8

Raman spectrum of EG<sup>900</sup>-1 contains the only G-line whereas spectra of the other exfoliated graphite samples contain D line as well. The Raman shift of EG<sup>900</sup>-3 G line is of 2727 cm<sup>-1</sup> and of D-line – is of 1581 cm<sup>-1</sup> and D/G intensity ratio is close to 1.2. The values of Raman shift of G and D line of the EG<sup>250</sup>-3 are the same but the ratio is about 0.5 and G line is narrower. That is the evidence that both samples contain not only graphite-like carbon but also an amorphous one and the amount on amorphous carbon is less for the sample prepared at higher temperature. Thus, the observed in EG-2, EG-3 and EG-4 samples graphite oxide being heated up decomposes with formation of amorphous carbon already at 250 °C. The exfoliation at higher temperature leads to amorphous carbon burn-out. So, amorphous carbon supplement the additional pores and providing high surface area.

### Conclusions

Pore structure of exfoliated graphite prepared in NO<sub>3</sub><sup>-</sup> containing intercalates was studied by means of nitrogen adsorption. It was shown, that electrochemically prepared samples possess the higher surface area and pore volume due to the presence of amorphous carbon covered EG<sup>T</sup> particles..

**Acknowledgments.** Authors are indebted to Dr. A.A. Eliseev for Raman spectroscopy investigations and Dr. V.A. Morozov for XRD experiments.

### References

- [1] Biloe S, Hauran S. Gas flow through highly porous graphite matrices. Carbon 2003;41:525-537.
- [2] Rodriguez-Rinoso F, Lopez-Gonzalez J. de D, Moreno-Castilla C. Adsorptive behavior of an exfoliated graphite. An. Quim. Ser.B 1981;77(1):6-18.
- [3] Toyoda M, Inagaki M. Heavy oil sorption using exfoliated graphite. New application of exfoliated graphite to protect heavy oil pollution. Carbon 2000;38:199-210.
- [4] Afanasov IM, Shornikova ON, Andeev VV, Lebedev OI, van Tendeloo G, Matveev AT. Expanded graphite as a support for Ni/carbon composites. Carbon 2009;47:513-518.