

PROPERTIES OF EXPANDED GRAPHITE PRODUCED FROM BRAZILIAN NATURAL CRYSTALLINE GRAPHITE

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Introduction

Graphite Intercalation Compounds (GICs) or expandable graphite are flake graphite stems from natural graphite mine (purity > 98%) intercalated with donor or receptor species. These materials are characterized by a charge transfer process between the intercalate and the graphite layers. A definite number of graphite layers separate intercalate layers, and the number of graphite layers between two intercalate layers is referred to as the stage of the compound. A variety of physical-chemical properties such as electrical conductivity and lattice dynamics depends on the stage structure (1).

Exfoliated graphite has an important role in industry, and it is usually produced by thermal treatment of GIC products. It is used in different applications such as thermal insulators, fire extinguishing agents, among others (2,3). Graphite sheet is used in sealing, packing, and in conductive resin composites, gaskets, electrodes, protective layers on carbon crucibles, lubricant supports, etc.

The several different intercalation compounds can be either donor or receptor species. Examples are: H₂SO₄, FeCl₃, Na-tetrahydrofuran (THF), K-THF, Co-THF, HNO₃, CuCl₂, ZnCl₂, HClO₄, H₃PO₄ or mixtures with reagents (6). The choice of the ideal intercalate depends on its purpose, because the final product characteristics vary considerably. Another important choice is the reaction precursor. The morphology, particle size, purity and other characteristics of the flake also influence the characteristics of the final product. The route used to obtain the intercalate graphite, as well as the choice of the reagents, determines how efficient the intercalation is, or which intercalation stage is obtained.

Experimental

In the present work, we compared two products from different intercalation processes, chemical and electrochemical syntheses, using Brazilian natural crystalline graphite. The chemical process was based on the oxi-reduction reaction of natural graphite (average particle size of 300µm, with purity up to 99.5%, NGL, Brazil) with HNO₃ 98wt% and

H₂SO₄ 98wt%. The other process was based on the electrochemical reaction between natural graphite (average particle size of 300µm with purity up to 99.7%, NGL, Brazil) and H₂SO₄ 98wt% as an electrolyte and intercalate (4,5). Both intercalated graphites were washed on the proportion 1g:3mL (graphite: water, 25°C) and expanded in a muffle at 900°C. The samples were milled to average particle size 150µm and characterized. The obtained samples are identified in the Table 1.

Table 1. Sample obtained in the different steps of the processes

Process step	Sample identification
Intercalated chemical	IC
Intercalated electrochemical	IE
Expanded chemical	EC
Expanded electrochemical	EE
Milled chemical	MC
Milled electrochemical	ME

X-ray diffractometry (RIGAKU Mod. DMAX 2.100 ULTIMA +) with Cu K α radiation, and monochromator on the secondary sheaf was used to compare the crystalline structure of the samples. The crystalline parameter Lc of expanded graphite was determined by Scherrer equation and the interlayer spacing (d₀₀₂) was determined from Bragg's equation. The Software FULL PROFF was used to identify the intercalation stages. The formula used was $lc = d_i + 3.35 \times (n-1) = 7.98 \text{ \AA}$, where lc= repetition period, d_i = inter-plain distance and n = intercalation stage. Polyethylene was used in measurement to protect the samples from decomposition by air moisture.

Particle size distribution of milled expanded graphites was measured by laser with equipment Malvern, considering the particle spherical. It can measure particles in the range from 0.05 to 704 µm.

The measure of the expansion indices (EI) was made weighing 1g of the intercalated graphite, which was heated up to 950°C during the necessary time to complete expansion, about 30 seconds. After that, the exfoliated graphite was carefully transferred into a graduated glass. The EI (mL/g) represents the volume of the exfoliated graphite of 1g of the intercalated graphite.

The purity of the samples was evaluated by an electron microprobe (Jeol JXA, model 8900RL) with an energy dispersive spectrometer (EDS).

Real density measures were obtained with a helium picnometer (Quantachrome). Textural characteristics of the samples were determined through nitrogen gas adsorption (machine type Autosorb - Quantachrome Nova 1200) at liquid nitrogen temperature. Specific surface area was obtained by the application of the Brunauer-Emmett-Teller (BET) equation. Nitrogen gas was used for 1,5 hours with a 23-point adsorption-desorption cycle. The samples dried at 100°C were outgassed at 150°C for 1 hour before each analysis. Experiments were made in triplicate.

Results and Discussion

X-ray diffraction patterns (Figure 1) show only 1 intercalation stage for the IC sample. Figure 2 shows that the IE has a mixture of stages 1 and 2, suggesting that the electrolytic intercalation supply a sample more stable than the chemical one. These measures were made on the first minutes after the reaction. Some intercalation studies [6] propose that fractional stage compounds are expected at the thermodynamic equilibrium for lamellar compounds. Inagaki & Wang [7] shows that the stage of the compound can be controlled changing the proportion of the reagents and the temperature of the synthesis. This fact demonstrates how unstable are these intercalated compounds.

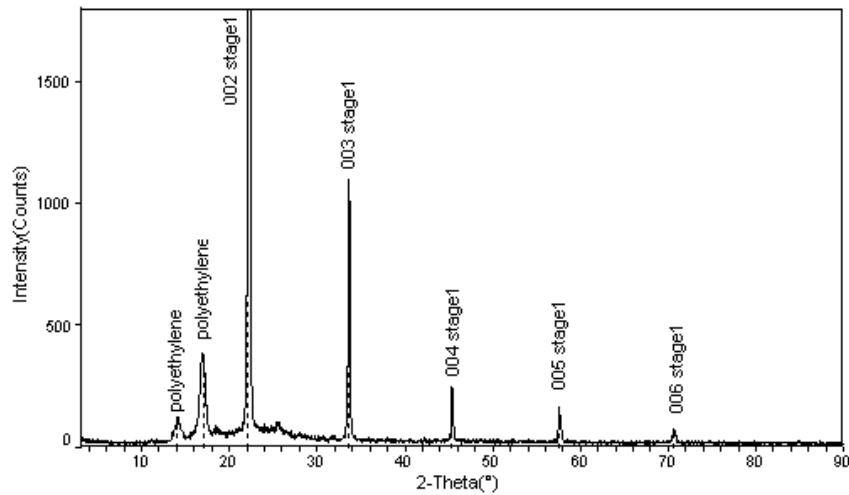


Figure 1. X-ray diffractogram of chemical intercalation graphite

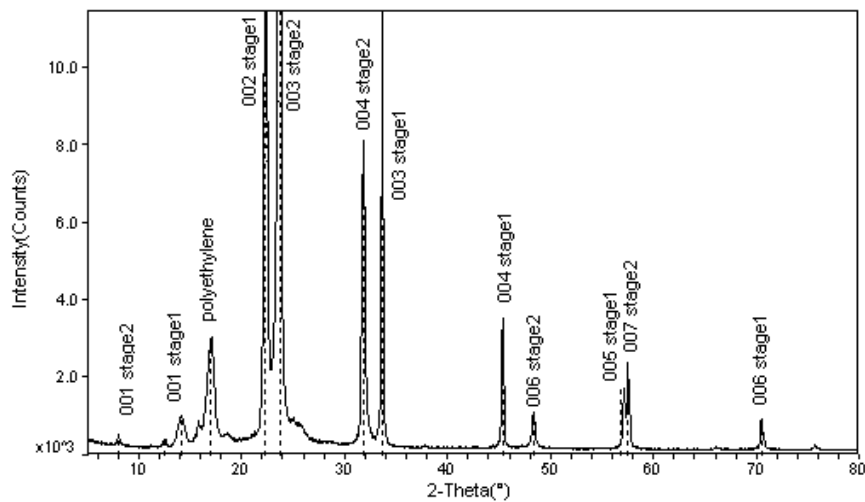


Figure 2. X-ray diffractogram of electrochemical reaction graphite

On the chemical intercalation, it is necessary the control of the proportion of the reaction components, the reaction temperature, the mixture route, the time of reaction and the control of the precursor characteristics (natural graphite), like the purity, particle size, moisture. On the electrochemical intercalation, it is also necessary the control of the current intensity of the reaction. All parameters have influence on the stages of the intercalated graphite.

Table 2 shows the Lc and d_{002} values of the milled samples MC and ME. The effect of the milling increase which the expansion index. Then, the sample ME, which obtained the higher expansion, has the small Lc because of the facility on the milling.

Table 2. Crystalline parameters

Sample identification	Lc (Å)	d_{002} (Å)
MC	659	3,3553
ME	349	3,3588

The EI are an important parameter to evaluate how efficient was the intercalation reaction. Table 3 shows the average EI results of the samples IC and IE. These measures are made immediately after washing and filtering the samples.

Table 3. Expansion Indices results measured at 950°C

Sample identification	EI (mL/g)
IC	250
IE	300

It is possible to observe that the IE sample present the higher value, and therefore, is more intercalated than the IC sample. We can observe by microanalyses that IC sample is more pure than IE and presents only stage 1 according the X-ray diffraction.

Figure 3 shows the distribution of the samples MC (Fig. 3a), ME (Fig. 3b) and the precursor (Fig. 3c), natural graphite. The precursor, which is a natural flake crystalline graphite from Nacional de Grafite Ltda, measured between 200 μm and 500 μm of diameter. The average size was 435 μm . The analysis of the particle size of the precursor is very important to the evaluation of the intercalation process. The samples milled presented similar distribution, with particles smaller than the precursor, since the milling process was the same for both graphites.

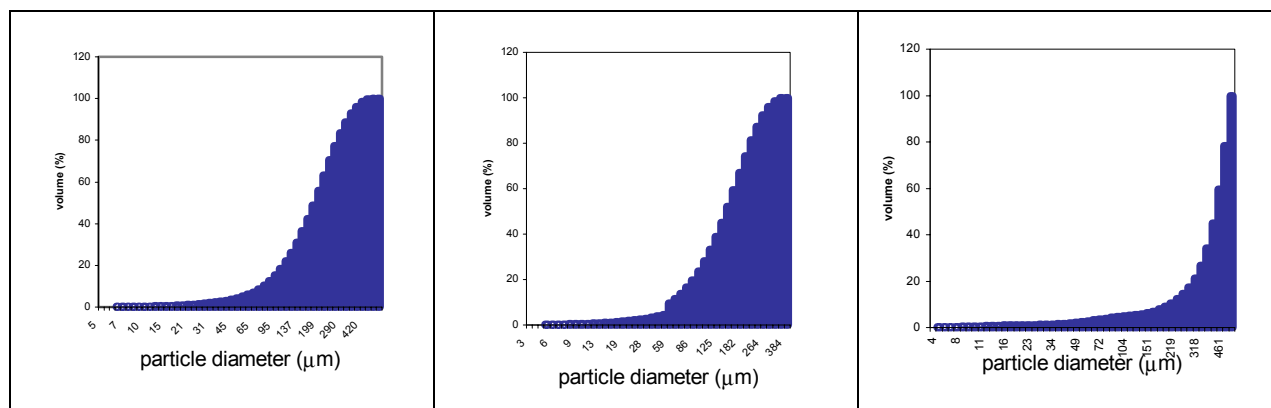


Figure 3 - Particle size distribution of the: (a) milling chemical expanded; (b) milling electrochemical expanded; (c) precursor natural graphite.

The results of the textural characteristics of the samples are on the Table 4. Figures 4 and 5 show the adsorption-desorption isotherms for the expanded and milled graphites, which presented type IV isotherm by BDDT⁸ classification, characteristic of mesoporous materials. The expanded graphites presented similar isotherms with hysteresis, but the EE is more porous and has larger surface area (Table 4). After milling, the graphites presented also similar isotherms, but without hysteresis. The porosity and surface area decreased after milling but the ME is still more porous that the MC. In this case, the milled graphite has a minor difficulty of desorption, verified by the small variation in adsorption and desorption pressure for the same amount of adsorbed gas.

Table 4 Textural characteristics of the exfoliated graphite

Sample	SSE (m ² .g ⁻¹)	Porosity (%)	BJH pore volume (10 ⁻³ .mL.g ⁻¹)	Real density (g.cm ⁻³)
EC	28	10	47	2.2
EE	49	15	79	2.2
MC	16	7	33	2.2
ME	23	10	50	2.2

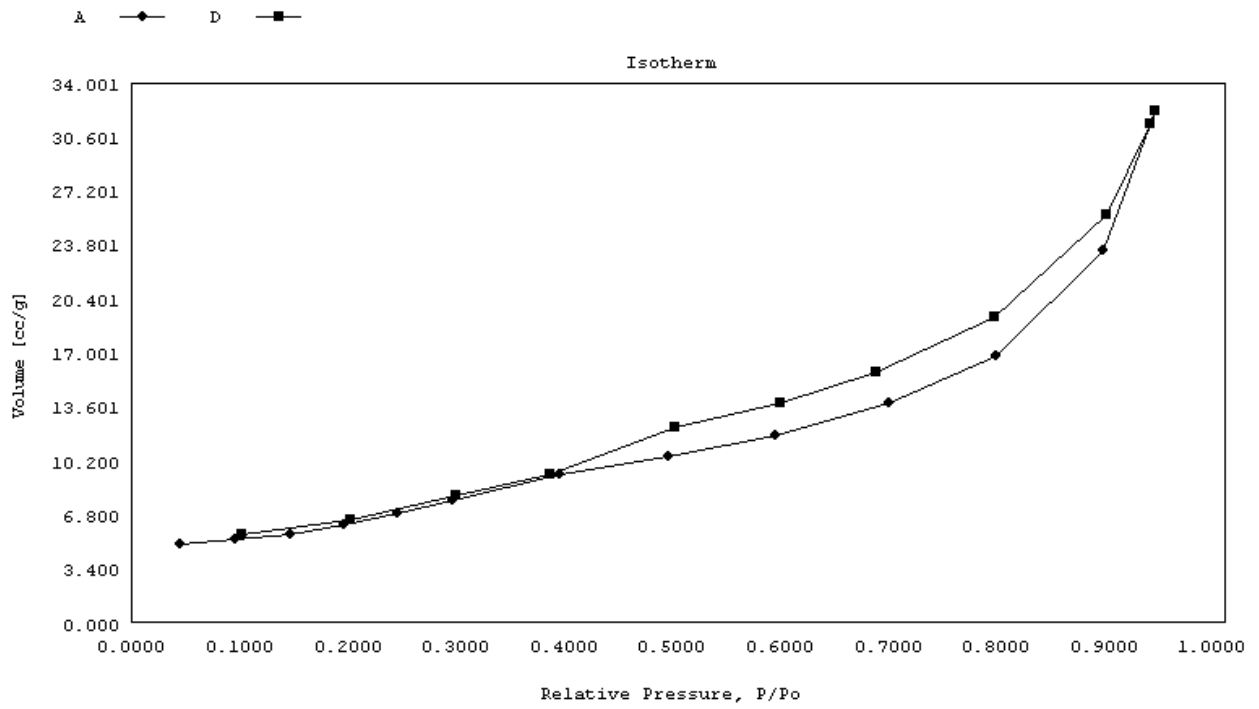


Figure 4 - Adsorption/desorption isotherms milled electrochemical graphite.

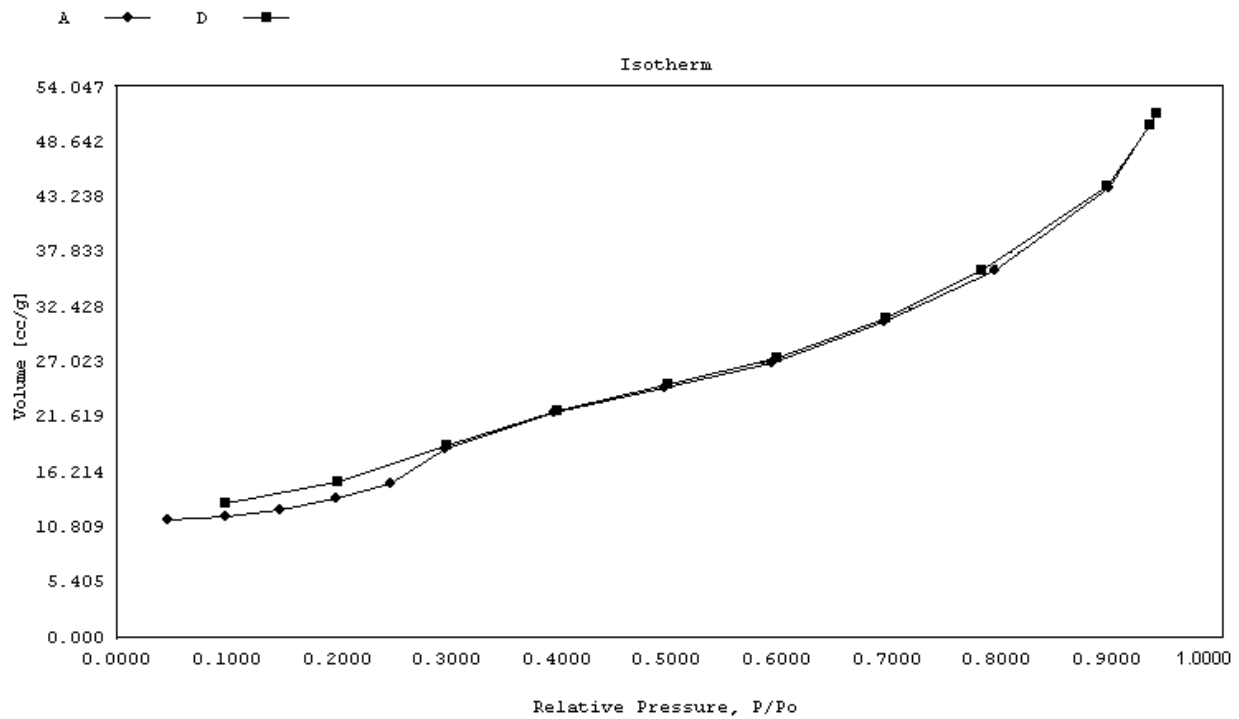


Figure 5 - Adsorption/desorption isotherms electrochemical graphite without milling.

Conclusions

With the same precursor, it is possible to obtain expanded graphite with characteristics distinct enough to be used in different applications. Both processes produced pure and expanded graphites, but EE is more porous, which is confirmed by its higher expansion index. After milling, both graphites present diminished surface area and porosity. All samples presented properties adequate to specific applications.

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