Graphite structural transformations during intercalation by HNO₃ and exfoliation

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ABSTRACT

Expandable graphite of two types was synthesized by (1) hydrolysis of graphite nitrate of II stage and (2) anodic polarization of graphite in 60% HNO₃. Exfoliated graphite samples were produced by thermal shock of expandable graphite samples in air at 900 °C. A comparative study of microstructural distinctions of both expandable and exfoliated graphite samples was carried out using X-ray diffraction, Raman spectroscopy, electron energy loss spectroscopy and high resolution transmission electron microscopy.

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Exfoliated graphite (EGᵀ), a product of expandable graphite (EG) thermal decomposition, is a low-dense material suitable for numerous applications: seals, sorbents, fillers for various composites, etc. [1]. EG is synthesized either by hydrolysis of graphite intercalation compounds ("chemical" approach) or by graphite anodic polarization ("electrochemical" approach). In the first case graphite nitrate of II stage is commonly used as EG precursor, whereas in the second – electrochemical oxidation in 10–60% HNO₃ solutions seems to be perspective [2]. The latter approach allows formation of "electrochemical" EGᵀ characterized by superior surface area [3] and tensile strength and elasticity of graphite foils [4] in comparison with these properties of "chemical" EGᵀ. These differences are obviously governed by both EG and EGᵀ microstructural peculiarities which are investigated quite scarcely.

In the present work natural purified graphite was treated with 98% HNO₃ to obtain graphite nitrate of II stage and then hydrolyzed by distilled water to result in "chemical" EG marked as EG-1. "Electrochemical" EG (EG-2) was synthesized by anodic polarization of pure graphite in 60% HNO₃ at stabilized current of 50 A/cm² density with a total electrical charge transfer of 1500 C/g. Both EG-1 and EGᵀ-2 samples were prepared by the thermal shock of the corresponding EG samples in air at 900 °C. We report a comparative study of graphite structural transformations during its chemical and electrochemical oxidation in HNO₃ in the mentioned conditions and consequent thermal exfoliation.

The samples were analyzed by XRD on an ARL X'TRA diffractometer (CuKα radiation, λ = 1.5418 Å, Peltier detector) in a 2θ range of 5–60° at a continuous scan rate of 2°/min. HRTEM experiments on the EGᵀ samples were taken on a Jeol 4000EX microscope at 400 kV. EELS spectra were recorded for EGᵀ-1, EGᵀ-2, natural graphite and amorphous carbon (prepared by short circuit and thermal evaporation in high vacuum) on a Philips CM30 FEG microscope equipped with a GIF 200 energy filter. Specimens for HRTEM and EELS were prepared by mechanical grinding in methanol and depositing the suspension on a holey carbon-coated copper grid. Raman spectra were recorded at room temperature with a LabRam HR-800 spectrometer using the 488 nm mode of Ar⁺ laser with a power of 0.01 mW.

The phase composition of EG-1 is represented by a mixture of graphite (d₀₀₂ = 0.336 nm) and graphite nitrate of VIII stage (ℓ = 3.130 nm) suggesting an incomplete acid deintercalation during hydrolysis of graphite nitrate of II stage (Fig. 1a) which is congruous with Iganaki data [5]. The phase composition of EG-2 is a mixture of graphite with an enlarged interlayer distance of 0.344 nm and graphite oxide (GO, d₀₀₁ = 0.670 nm) (Fig. 1b). GO formation during graphite anodic polarization in 60% HNO₃, i.e. very close to HNO₃ intercalation threshold [2], should be attributed to hydrolysis of in situ obtained graphite nitrate and carbon oxidation with the formation of covalent C–O bonds. The development of entirely turbostratic structure (dₐ₀₂ = 0.344 nm) in EG-2 as the result of electrochemical treatment is accompanied by 10 times reduction.
of graphite crystalline size \( L_c \) estimated using Scherrer equation. In contrast, graphite interlayer distance and crystalline size in "chemical" sample are only slightly alternated (Table 1).

Non-essential graphite lattice damage by "chemical" treatment is confirmed by Raman spectroscopy data: the narrow G lines are observed in spectra of both natural graphite and EG-1 (Fig. 2a and b). The appearance of the line at \( \sim 1610 \text{ cm}^{-1} \) in the spectrum of EG-1 could be related to a split of the G mode upon intercalation arising primarily from the symmetry changes at a graphitic "boundary layer" adjacent to an intercalant layer [6]. The broadening and the shift of G line to higher frequency and the appearance of broad D line at 1350 \( \text{cm}^{-1} \) in EG-2 spectrum (Fig. 2c) point to intense formation of structural defects and dramatic break of the original graphite domains into several smaller ones during graphite anodic polarization in 60% HNO\(_3\) which is in a good agreement with the crystalline size reduction deduced from the XRD data.

Thermal shock of EG flakes promotes their expansion and dramatically changes their shape and size. Exfoliated graphite is a mass of chaotically oriented worm-like particles with a bulk density of 2.2 g/l (EGT-1) and 1.0 g/l (EGT-2). The lower bulk density of EGT-2 should be accounted for the higher disjoining pressure created by water and CO\(_2\) as the products of GO thermal decomposition in the case of EG-2 exfoliation than the pressure of water and NO\(_x\) responsible for EG-1 exfoliation [7].

Raman spectrum of EGT-1 contains only narrow G line (Fig. 2d) suggesting an almost perfect graphite microstructure. The broadened asymmetrical G line and the wide D line in the EGT-2 spectrum (Fig. 2e) are indicative for nanocrystalline graphite and a high concentration of defects in the sample. In order to quantify the crystalline/amorphous ratio in EGT-1 and EGT-2 EELS spectra of the carbon K edge of the samples (Fig. 3a) were interpreted as a linear combination of the two normalized reference spectra of graphite and amorphous carbon, taking into account the background and multiple scattering [9]. The analysis revealed that the content of amorphous carbon is less than 0.5 wt.% in EGT-1 whereas it appears to be around 60 wt.% in EGT-2. Moreover, the shift and the intensity decrease of the plasmon peak (24–28 eV) in the low-loss spectrum of EGT-2 (Fig. 3b) also point to a decrease in the crystalline sp\(^2\) content [8]. The shift of the peaks at 6–8 eV (Fig. 3b) could be relevant for the different colour of the samples: EGT-1 is grey while EGT-2 is black that is again relevant to the presence of amorphous carbon in the latter sample.

HRTEM analysis confirmed a close to ideal crystalline graphite microstructure of EGT-1. It consists of >30 nm-thick sheets with a \( d_{002} \approx 0.336 \text{ nm} \) where planarity of graphene layers is maintained (Fig. 4a) though a few graphenes are delaminated apparently as the result of exfoliation. On the contrary, "electrochemical" EGT is a highly defective material with a low crystalline fraction visualized by imperfect fringes in Fig. 4b and c. Of the 5–10 nm defective sheets with an inter-

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d_{002}, \text{nm} )</th>
<th>( L_c, \text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural graphite</td>
<td>0.335 ± 0.01</td>
<td>70 ± 10</td>
</tr>
<tr>
<td>EG-1</td>
<td>0.336 ± 0.01</td>
<td>55 ± 7</td>
</tr>
<tr>
<td>EGT-2</td>
<td>0.344 ± 0.01</td>
<td>7 ± 2</td>
</tr>
</tbody>
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Fig. 1 – XRD patterns of expandable graphite samples: EG-1 (a) and EG-2 (b). Indexes C, NG VIII and GO correspond to graphite, graphite nitrate of VIII stage and graphite oxide respectively.

Fig. 2 – Raman spectra of natural graphite (a), expandable graphite (b and c) and exfoliated graphite samples (d and e).
layer spacing of ∼0.339 nm are observed in EG^T-2 which comes to ∼60% of turbostratic graphene planes according to Bacon equation. A variety of defects is present in the sample: stacking faults, delamination strands, misorientation bands and local alteration of highly anisotropic to isotropic texture. Moreover, 1 nm-thick amorphous carbon layers cover the EG^T-2 sheet (Fig. 4c). One should take into account that despite some delaminated graphenes observed in Fig. 4a no buckled planes and mentioned defects were detected in EG^T-1; thus they are typical neither for initial graphite nor for “chemical” material and cannot arouse through the specimen preparation for HRTEM but are characteristic only to “electrochemical” EG^T. The observed features in EG^T-2 apparently originate from the thermal decomposition of GO present in EG-2. It is accompanied by CO₂ release leaving behind vacancies and topological defects in graphene sheets [7]. The coalescence of the vacancies and the accumulation of defects result in final disruption of the graphene layers planarity and partial amorphization of the sample.

To sum it up, we showed that intercalation with 98% HNO₃ followed by hydrolysis leads to graphite nitrate of VIII stage formation and non-essential graphite lattice damage; the afterwards obtained exfoliated graphite consists mostly of well-ordered sp² carbon with an interlayer distance of 0.336 nm. In contrast, anodic polarization in 60% HNO₃ results in a dramatic break of original graphite domains and graphite oxide formation which is responsible for amorphization of the later on obtained exfoliated graphite consisting of the 5–10 nm-thick faulted graphite sheets covered by ∼1 nm-thick amorphous carbon layers. These microstructural peculiarities would be obviously crucial for the physicochemical properties of “electrochemical” EG^T and related materials: sorption ability, thermal and electrical conductivity, etc.

Fig. 3 – Carbon K edge core-loss (a) and low-loss (b) EELS spectra of exfoliated graphite samples.

Fig. 4 – HRTEM images of exfoliated graphite samples: EG^T-1 (a) and EG^T-2 (b and c).

REFERENCES


