

EVOLUTION OF POROUS STRUCTURE AND THERMAL PROPERTIES OF EXPANDABLE AND EXPANDED GRAPHITE RESULTED BY GRAPHITE OXIDATION

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Introduction

Expanded graphite (EG) is a well-known graphite material that found great application for production non-asbestos packing materials and heat-distributing materials¹⁻⁴. The structure and properties of expanded graphite depend on the way of expandable graphite preparation and on exfoliation conditions¹⁻². Despite numerous researches devoted to correlation of GIC stage number and graphite materials properties, there is still a few works about properties of overoxidized graphite although these materials demonstrate unique high surface area and low thermal conductivity. The aim of present work was to find out the correlation between the depth of graphite oxidation and properties of graphite materials.

Materials and Methods

Natural flaky graphite (200-300 μm) was subjected to long-term treatment in 60% HNO_3 using chemical and electrochemical techniques. The depth of graphite matrix oxidation in chemical synthesis (CS) was varied by its duration and was 1-5 weeks, in electrochemical synthesis (ES) – by the specific quantity of electricity passed through graphite (Q) from 500 to 3000 C/g. After synthesis, expandable graphite was washed by water excess until neutral pH of filtrate was achieved and dried at room temperature for at least 24 hours. Exfoliation was carried out at T 250 and 1000 $^\circ\text{C}$ in air. The prepared EG samples are further denoted as CS-duration (weeks)-T and ES-Q-T. XRD, Raman spectroscopy, SEM, nitrogen adsorption, DSC and laser flash analysis were applied for all the samples.

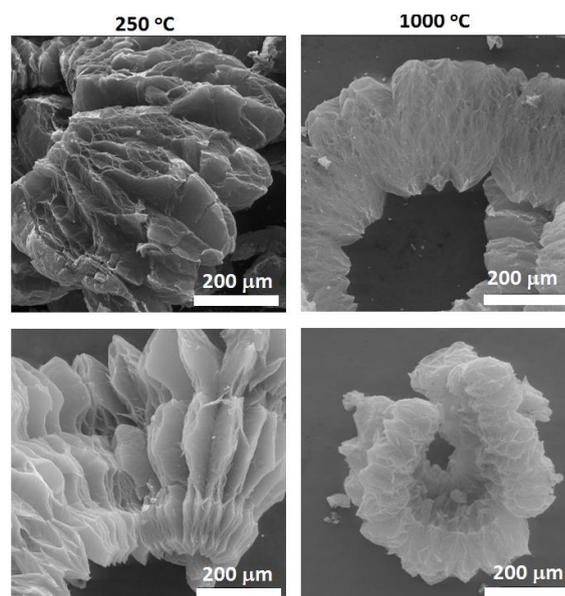
Results and Discussion

According to XRD, structure of all chemically prepared expandable graphite samples is represented by defective graphite while electrochemically prepared samples contains admixture of graphite oxide since $Q = 1500$ C/g. This is why electrochemically prepared expandable graphite exothermally decomposes and expands as low as 250 $^\circ\text{C}$ giving EG with bulk density 5.1-10 g/l in contrast to CS samples (**Table 1**). EG samples has a worm-like shape in all cases. Graphene packs are separated with macropores (**Figure 1**) for both CS and ES samples but for ES samples thickness of the “packs” is less and distance between is higher.

Besides the peaks referred to G-mode, in Raman spectra of ES-Q-T samples when $Q \geq 1500$ C/g, D-mode corresponding to defective graphite or even soot is observed. Soot is a result of graphite oxide thermal decomposition and its amount decreases with an increase of exfoliation temperature that is resulted in decrease of D-mode intensity for ES-Q-1000 samples. CS samples obtained at 250 $^\circ\text{C}$ was not used in further work because were not capable to be compacted.

Table 1. Characteristics of initial* and compacted EG

Sample	d*	CY*	C _p	λ	S	V,
	g/l	%	J/g/K	Wt/m/K	m ² /g	ml/g
CS-I-250	80	85	-	-	<5	-
CS-II-250	60	85	-	-	<5	-
CS-III-250	60	84	-	-	<5	-
CS-IV-250	50	83	-	-	<5	-
CS-V-250	55	84	-	-	<5	-
CS-I-1000	2.7	52	0,780	3.9	20	0.08
CS-II-1000	3.5	52	0,750	3.9	25	0.08
CS-III-1000	3.5	52	0,705	3.6	25	0.08
CS-IV-1000	3.4	56	0,705	3.0	30	0.09
CS-V-1000	3.8	58	0,705	2.8	30	0.09
ES-500-250	10	84	0,805	4.1	20	0.07
ES-1000-250	5.3	84	0,805	2.2	40	0.08
ES-1500-250	5.1	84	0,790	1.8	150	0.80
ES-3000-250	5.9	82	0,780	1.4	140	0.80
ES-500-1000	1.1	61	0,780	4.5	60	0.10
ES-1000-1000	1.0	64	0,705	4.3	80	0.12
ES-1500-1000	1.1	59	0,690	3.5	100	0.60
ES-3000-1000	1.2	61	0,680	3.0	90	0.40

**Figure 1. SEM images of EG samples CS-IV-T (upper) and ES-500-T.**

Heat capacity, thermal conductivity and pore structure were studied for EG samples compacted in discs with a density of 1 g/cm³ (**Table 1**). Generally, surface area and pore volume are higher for ES samples and decrease with temperature because of burning-out of amorphous carbon (soot). Heat capacity (C_p) of natural graphite and EG prepared by GIC exfoliation is about 0.8 J/g/K while C_p of both CS and ES samples decrease significantly to 0.7 J/g/K for more than III week or 1000 C/g.

Thermal conductivity for EG samples prepared at 1000 °C varies from about 3.0 for ES-3000-1000 and CS-V-1000 to 3.9-4.5 for ES-500-1000 and CS-I-1000 respectively. ES-Q-250 samples demonstrate 2 times lower thermal conductivity. Probably, the large amount of amorphous carbon leads to multiplication of particle-particle borders where heat could dissipate.

Conclusions

Microstructure, porous structure, heat capacity, and thermal conductivity for all EG samples were determined and correlation between the synthesis conditions and properties was estimated. It was shown that deep graphite oxidation significantly changes graphite structure: leads to development of porous structure, mostly mesoporous; decrease of heat capacity and variable thermal conductivity.

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References

1. Afanasov I.M., Shornikova O.N., Kirilenko D.A., Zhang L., Verbeek J., I.I. Vlasov, V.V. Avdeev, van Tendeloo G. (2010). Graphite structural and morphological transformations during intercalation exfoliation. *Carbon*, 48, 1858-1865
2. Chen P.-H., Chung D.D.L. (2014). Thermal and electrical conduction in the compaction direction of exfoliated graphite and their relation to the structure. *Carbon*, 77, 538-550
3. Wang L.W., Metcalf S.J., Critoph R.E., Thorpe R., Tamainot-Telto Z. (2011). Thermal conductivity and permeability of consolidated expanded natural graphite treated with sulphuric acid. *Carbon*, 49, 4812 – 4819
4. Wang L.W., Tamainot-Telto Z., Metcalf S.J., Critoph R.E., Wang R.Z. (2010). Anisotropic thermal conductivity and permeability of compacted expanded natural graphite. *Applied Thermal Engineering*, 30, 1805-1811