

THE INCORPORATION OF SF₆ INTO GRAPHITE AND OTHER MATERIALS*

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The formation of intercalation compounds from sulfur fluoride SF₆ and layered substrates was observed. The process is accelerated if the substrate had been preexposed to SF₆ partly decomposed by electric spark discharges. The amount of intercalated SF₆ decreases in the series graphite > molybdenum disulfide > boron nitride. The promotion effect is explained by exfoliation of the substrate due to highly reactive fission products of SF₆.

Key words: Intercalation compounds; Graphite; Sulfur fluoride; Boron nitride.

The process of intercalation is based on the incorporation or penetration of small mobile particles (ions, small molecules) into a host matrix possessing regularly spaced voids, channels, or planes. As the host matrices, many inorganic substances such as lamellar dichalcogenides, zeolites, or graphite are known (see ref.¹). Graphite intercalation compounds (usual abbreviation GIC) are known for 150 years already (*e.g.*, see ref.²). In general, their composition is given as the number of substrate (sometimes called *host*) formulas per 1 particle of intercalated species, *e.g.*, C₆Li, *etc.* Among them, two families are interesting. The first of them is represented by GICs of anions, mostly fluorinated, such as AsF₆⁻, PF₆⁻, and others. Their electric charge is compensated by injection of holes into the π -electron system of graphite, and therefore they may be considered as electron acceptors. The other group includes the GICs containing electrically neutral particles; among them a variety of fluorinated non-metals and semi-metals can be found such as WF₆, UF₆, and even xenon fluorides. Nothing is known on intercalation of sulfur hexafluoride, SF₆, until now. According to Bartlett², however, the molecule of SF₆ is quite inert and does not have enough affinity to electrons so that the

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interaction of it with the graphene layers would not yield enough energy necessary to increase the interlayer distance in the van der Waals gap of graphite. In other words, it does not seem probable.

The aim of this paper was to investigate whether sulfur hexafluoride can intercalate into layered compounds with some promotion, *e.g.*, by electric discharge.

EXPERIMENTAL

Materials

Graphite CR-5 (micromilled, average particle size 5 μm , Netolice mine, Czech Republic) was used as the most important intercalation substrate. Together with it, also hexagonal boron nitride h-BN (Prague Institute of Chemical Technology) and layered molybdenum disulfide MoS_2 (natural powder known as solid lubricant MOLYKO delivered by KORAMO Kolín, Czech Republic) were used for comparison. The average particle size, 1.2 μm , and specific surface area, 1.1 $\text{m}^2 \text{g}^{-1}$, were estimated for boron nitride by means of FRITSCH Particle Sizer Analysette 20. This measurement was impossible in case of MoS_2 , and an approximate value 2 μm is the only one available from electron microscopy. Gaseous SF_6 (LINDE – Technoplyn, Prague) was used as received.

Methods and Instrumentation

The exposition of materials to spark discharges was performed in a cylindrical discharge chamber made of aluminosilicate glass SIMAX and organic poly(methyl metacrylate) (PMMA) glass of the 1 l volume (approximately), equipped with an automobile spark plug. The spark plug was fed from a *d.c.* voltage source (25 kV) *via* an R–C network (10 $\text{M}\Omega$ in series, 1 000 pF parallel to the gap); the breakdown voltage in SF_6 was 16 kV approximately. The total energy absorbed by the discharge reached 20 to 40 kJ in 1 or 2 h interval. The chamber was filled at atmospheric pressure and temperature 20 to 22 $^\circ\text{C}$, and it was not controlled during the experiment.

The rate of SF_6 sorption was measured in a simple volumetric apparatus using samples both as received and pre-exposed to spark discharges. The vessel of known volume containing the sample was evacuated, and then SF_6 at laboratory pressure was introduced into it. The pressure was kept constant in the course of experiment, and the volume changes were recorded by means of a gas burette. Furthermore, the sorption was monitored gravimetrically by the mass change of the sample extracted from the spark chamber at the end of exposition to SF_6 . After the experiment, the samples lost their weight in the open air due to the desorption of SF_6 almost down to the original mass.

The formation of fission products in the discharge chamber was checked by gas chromatography (CHROM-5, Laboratorní přístroje, Czech Republic). The chemical changes in graphite substrate were evidenced by X-ray diffraction analysis.

RESULTS

X-Ray Diffraction

The X-ray diffraction patterns consisted of (002) graphite reflection line mainly. This line underwent splitting into two lines if graphite was exposed to SF_6 (see Fig. 1). The

appearance of a peak indicated the formation of a phase with interlayer spacing increased by 6.9 pm.

Sorption and Desorption of SF₆

In general, the sorption of SF₆ in graphite was rather fast and a limiting value was reached safely within one hour. In some cases, a short induction period at the beginning of the experiment appeared. Such a behaviour is shown as an example in Fig. 2 where the volume uptake is plotted against square root of time, $t^{1/2}$.

The desorption of SF₆ started immediately when the sample had been withdrawn from the reaction chamber and was accomplished within one or two hours.

Kinetics of SF₆ Sorption

According to the generally accepted model of intercalation, the sorption should be controlled by diffusion in the solid state³. However, the low uptake rate at the very beginning should be treated in another way. As an approximation, we have introduced the duration of induction period, t_0 , such that the sorption rate equals to zero for time $t < t_0$ and obeys the solution of 2nd Fick law in which the real time is replaced by the shifted time $(t - t_0)$, and the sorption begins exactly at time t_0 .

Therefore, the relative SF₆ uptake M/M_∞ is then governed (for time $t > t_0$) by the relation

$$\frac{M}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{i=1}^{\infty} \frac{1}{i^2} \exp [-D (i\pi/\rho^2) (t - t_0)] \quad (1)$$

which, for a sufficiently long time interval, turns into an approximate solution

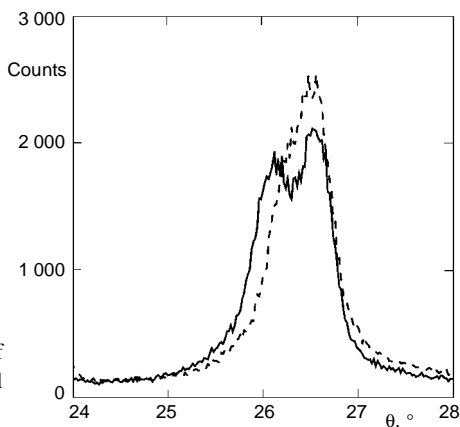


FIG. 1
X-Ray diffraction line of (002) reflection of both fresh (dashed line) and SF₆ exposed (full line) graphite. Radiation: CuK α

$$1 - \frac{M}{M_\infty} \approx \frac{6}{\pi^2} \exp\left(-D \frac{t \pi}{\rho^2}\right) \quad (2)$$

or

$$\ln\left(1 - \frac{M}{M_\infty}\right) \approx \ln \frac{6}{\pi^2} - D \frac{t \pi}{\rho^2} = -0.498 - ct \quad (2a)$$

from which apparent rate constant $c = D\pi/\rho^2$ can easily be estimated as a slope of plot according to Eq. (2a). Under the circumstances, the whole bulk of particles is saturated by the intercalated species. Therefore, this method of estimation of the diffusion coefficient was preferred in this paper as it does not reflect so deeply the surface defects in the grains of the host substrate.

On contrary, the well-known Cottrell formula in the modified form

$$\frac{M}{M_\infty} = K \sqrt{t - t_0} \quad (3)$$

is valid for short time ($t - t_0 \rightarrow 0$, $t - t_0 > 0$), the value K being given by the particle radius ρ , density d , and diffusion coefficient D :

$$K = \frac{6}{\rho} \sqrt{\frac{D}{\pi}}. \quad (4)$$

Formula (3) should be valid for spherical particles and time sufficiently shorter than the some threshold time t_c between the validity domains of Eqs (2) and (3). In this case,

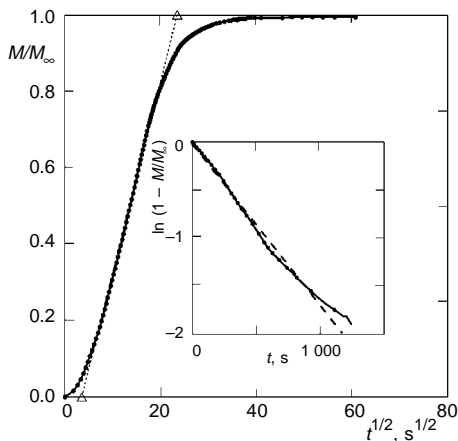


FIG. 2

Example of SF_6 uptake according to Eqs (2) and (3) for the sample of graphite CR-5 pre-exposed to electric discharge in SF_6 . Solid line and points: experimental data. Dashed line: values according to Eq. (3). In the insert: the same data expressed according to Eq. (2a). Dashed line: linear fit of the data

only a thin layer under the particle surface is penetrated by the intercalated species, and this layer can be considered as a quasiplanar one. The threshold time t_c is related to particle radius ρ and diffusion coefficient D by the approximate relation

$$D(t_c - t_0)/\rho^2 \approx 1 \quad (5)$$

An example of SF₆ uptake is shown in Fig. 2 where the ratio M/M_∞ is plotted against square root of time ($t^{1/2}$) on horizontal axis, and in semilogarithmic plot against time (t) according to Eq. (2a) as an insert. As we can see, Eq. (1) describes the behaviour sufficiently in the whole time range if time is reasonably longer than the duration of induction period, $t_0 \approx 50$ s. However, Eq. (3) is fulfilled for shorter time ($t < 600$ s approximately) as it is shown by a dashed curve in Fig. 2. For longer time, Eq. (2) offers a reasonably good approximation (see the insert in Fig. 2).

Assuming the average particle radius of 2.5 μm of graphite powder CR-5, the values $t_0 = 12.3$ s and $t_c = 580$ s were found from the intercepts of a tangent at the point of the highest slope with the horizontal axis and with the horizontal asymptote, respectively (see Fig. 2). Assuming the density of graphite 2 200 kg m⁻³, the apparent coefficient of SF₆ diffusion in graphite, $D_{\text{SF}_6} \approx 0.9 \cdot 10^{-14}$ m² s⁻¹, was estimated using Eq. (5). This is in a reasonable agreement with the data in Table I which were obtained by means of Eq. (2a).

The sorption of SF₆ by all three intercalation substrates was evaluated using Eq. (2a). The data are summarized in Table I where diffusion coefficients were calculated from apparent rate constant c using particle radius of the host substrates.

DISCUSSION

The Influence of Electric Discharges

As the data in Table I show, the process was faster and proceeded to a greater depth final concentration if the substrate had been pre-exposed to electric spark discharges which had generated fission products such as SOF₂, SO₂F₂, HF, CF₄, and others. The origin of oxygen for the former ones is expected to be residual humidity and air content in the discharge chamber. Also any reaction with PMMA organic glass cannot be entirely excluded.

We suppose that the decomposition products of SF₆ are chemically more active. Therefore, they occupy the orifices of interlayer gaps (called usually van der Waals gaps), enter them, and they act as a cleavage (or exfoliation) agents increasing the interlayer gap. The mobility of SF₆ increases due to the enlarged van der Waals gaps, while the final amount of intercalated species is influenced by opening greater number

of those gaps. In this way, the increased interlayer gap and pillaring effect of active molecules have promoting effect on intercalation (both equilibrium and diffusion rate) of chemically inert SF_6 .

The Influence of the Substrate

The intercalation of SF_6 proceeds in all three layered substrates and is promoted by their pre-treatment by decomposition products of SF_6 . There is a small difference between graphite, hexagonal h-BN, and MoS_2 which indicates that the role of electronic interactions between the substrate and intercalated particles in intercalation compounds of spherical non-metal fluorides does exist but is not the prevailing one. Apparently, rather inert particles of SF_6 do not need much interaction with the substrate framework either for the intercalation equilibrium or kinetics if there is enough space to accommodate them. Due to non-polar nature of SF_6 , the penetration of its molecules should be easier for a non-polar graphite than for boron nitride which is created by covalent bonds without the mobile π -electron orbitals and with some degree of B–N bond polarity. Thus, the mobility and final concentration of SF_6 are the highest in graphite. Rather small increase of layer spacing along *c*-axis (as indicated by the shift of (002) diffraction line) is in agreement with quite small interaction and related interaction energy as should be expected from the properties of SF_6 . Theoretically, if all gaps accept intercalate particles, then one sufficiently small particle of intercalate requires usually 6 or 8 atoms of carbon (according to geometry of the system). Therefore, the numbers in Table I indicate that only small amount of interlayer gaps are occupied by SF_6 . This phenomenon is called stageing¹.

TABLE I
Sorption of SF_6 by various substrates

Substrate	ρ , μm	n^a	c , s^{-1}	$D_{\text{SF}_6} \cdot 10^{14}$, $\text{m}^2 \text{s}^{-1}$
Graphite, as received	2.5	84 : 1	0.021	4.2
Graphite, discharge exposed	2.5	67 : 1	0.035	7.0
h-BN, as received	0.55	232 : 2	0.0133	0.13
h-BN, discharge exposed	0.55	80 : 1	0.023	0.22
MoS_2 , as received	1	197 : 1	0.02	0.6
MoS_2 , discharge exposed	1	45 : 1	—	—

^a Formula units of substrate per 1 mol of SF_6 (as formula units, MoS_2 , BN and C are considered).

SYMBOLS

c	apparent rate constant according to Eq. (2a), s ⁻¹
d	density of the host substrate, kg m ⁻³
D	diffusion coefficient of SF ₆ in the host substrate, m ² s ⁻¹
K	slope of Cotrell plot according to Eqs (3) and (4), s ^{-1/2}
M, M_{∞}	volume of SF ₆ sorbed at time t and its limiting value at $t \rightarrow \infty$
t	time, s
t_0	duration of initial induction period, s
t_c	threshold time between validity of Eq. (1) for spherical diffusion and Eq. (3) for quasi-planar diffusion, s
ρ	average particle radius, m
θ	X-ray diffraction angle, °

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