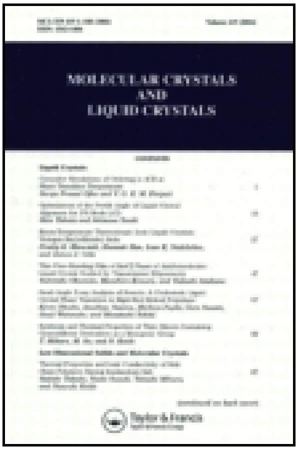

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ELECTROCHEMICAL REDOX CAPACITY OF THERMALLY EXFOLIATED GRAPHITE IN SULFURIC ACID

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Abstract Thermally expanded graphite (TEG) was prepared from graphite hydrogensulfate, 1st and 2nd stage, at 550 °C. Surprisingly, the intercalation redox capacity and the cyclic voltammetric (CV) profiles in 18 M H_2SO_4 do not change significantly with respect to pristine graphite. CV in 10 M H_2SO_4 revealed a higher concentration of redox active surface groups. This is attributed to an oxidative attack by SO_3 in the course of the exfoliation process.

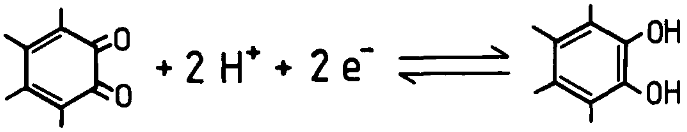
INTRODUCTION

Graphite intercalation compounds (GIC's) are known to be thermally instable. Upon rapid heating, release of the intercalated species and a strong expansion of the solid along the c-axis by a factor of 3 to 300 is attained. This irreversible exfoliation was proposed as early as 1916 for the manufacture of thermally expanded graphite (TEG).[1] It has found widespread application as a material for gaskets, seals and packings due to its high flexibility, thermal stability and lubricity. Since 1964 a reversible expansion at lower temperatures is known.[2]

We report our results of a research into the electrochemical characterization of TEG. Nearly nothing is published in this field. Electric conductivity is found to increase slightly along c, and to decrease parallel to a.[3,4] Two types of reversible redox reactions are known for graphite,[5] namely for the anodic intercalation of anions and their cathodic release as a bulk process:

$$C_x + 3\,H_2SO_4 \rightleftharpoons [C_x^{+}HSO_4^{-} \cdot 2\,H_2SO_4] + e^{-} + H^{+} \qquad (1)$$

and the redox transition of o-quinoid surface groups:



(2)

These redox processes are located at the graphene planes and at the edge of planes of the crystal, respectively.

EXPERIMENTAL

Graphite intercalation compounds were prepared by galvanostatic intercalation of natural graphite flakes ("Grossflocke", Kropfmühl AG, Germany) in a bed electrode.[6] The cylindrical cell (d= 5 cm) was filled with 42 g graphite flakes. Geometric current density was 5 mA cm^{-2}. Stage II of GIC with the composition $C_{48}HSO_4 \cdot 2\ H_2SO_4$ was obtained in 12 M H_2SO_4 using a flow through bed electrode, whereas stage I, $C_{24}HSO_4 \cdot 2\ H_2SO_4$, was prepared in 18 M sulfuric acid. The GIC's were stored under vacuum without any washing. Process of exfoliation was performed in a tube furnace at 550 °C under Ar atmosphere. The GIC samples inserted in quartz boats were heated in two ways: A) short treatment during 1 min at 550 °C; B) linear heating up by 10 °C min^{-1} from 20 °C to 550 °C and remaining there for 1 min.

Cyclic potentiodynamic experiments were performed at 20 °C under Ar with samples of about 5 mg TEG inserted in a pocket made from Pt/Ir-grid (1024 mesh cm^{-2}). Pristine natural graphite was used as reference. Industrial products, eg. Sigraflex (Sigri AG) and Grafoil (Union Carbide) were shredded from the foils. Hg/Hg_2SO_4(1 M H_2SO_4) was used as reference electrode, (+674 mV vs. SHE), potentials "U_S". Electrochemical equipment consisted of a potentiostate with integrated scan generator Heka, model PG 28. Because of the unknown area of graphite electrodes, a mass specific current i (A g^{-1}) is used instead of the area specific current density.

RESULTS AND DISCUSSION

The exfoliation temperature of 550 °C, which was employed in this work, was distinctly below the industrially used level of 1200 °C.[1,7] However, it is appropriate for the expansion of graphite hydrogensulfate.[8,9] The experimental weight losses were about 20% above the value which can be calculated after

$$[C_x^+HSO_4^- \cdot 2\ H_2SO_4] + H_2O \rightleftharpoons C_x\text{-}OH + 3\ H_2SO_4 \qquad (3)$$

This can be assigned to ahdering sulfuric acid. However, if the GIC (1st stage) contains 9 mole water in addition, as derived indirectly in[10], an exact mass balance is attainable. Volume expansion f= V/V_0 was found to be in the order of 5-10, in contrast to f=300, obtained at 1200 °C. The shock heated products led to higher expansions.[11]

A typical SEM micrograph of TEG is shown in Fig. 1, which reveals the wellknown[11] porous honeycomb microstructure of TEG. Lamellar thickness goes down to about 0.5 μm, corresponding to about 10^3 graphene layers.

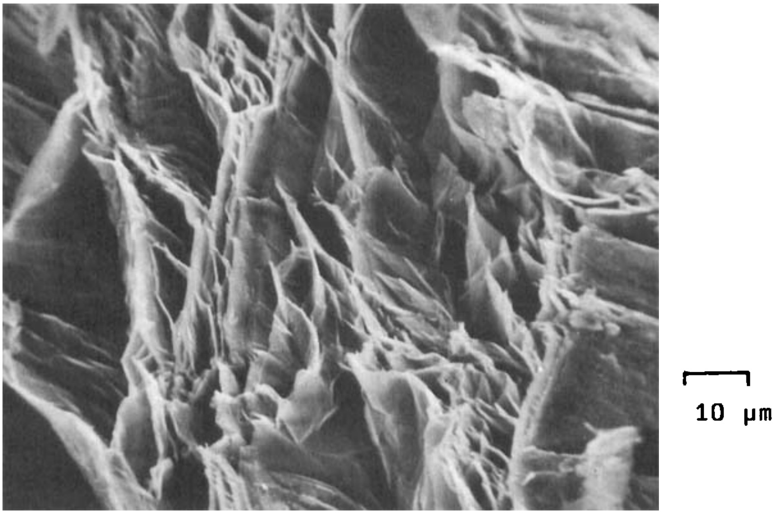


FIGURE 1 SEM of TEG (sample 5, made from 2nd stage GIC).

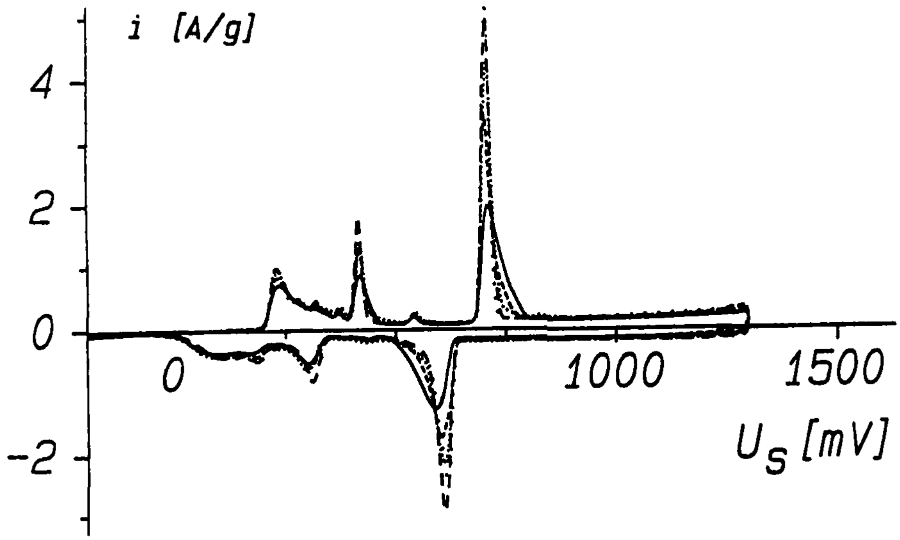


FIGURE 2 CV in 18 M H_2SO_4, v_s= 1 mV s^{-1}, 3rd cycle with TEG's, sample 1(———), 2(·········), 3(– – – -), 4(– – –) and 5(· • · · ·).

TABLE 1 Current efficiency α and cathodic mass utilization μ for pristine graphite and TEG samples from CV-measurements (3rd cycle, 1 mV s^{-1}) in 18 M H_2SO_4 (cf. Fig.2) and 10 M H_2SO_4 (cf. Fig.3). μ_{cath} refers to the 1st stage C_{24}^+ (18 M H_2SO_4) and 2nd stage C_{48}^+ (10 M H_2SO_4), respectively.

Sample	GIC stage	Exfol. meth.	18 M H_2SO_4		10 M H_2SO_4	
			α	μ_{cath}	α	μ_{cath}
Reinstflocke			1.00	1.09		
Grossflocke1)					0.92	0.86
TEG,sample 1	1	A	0.95	0.94	0.90	0.91
TEG,sample 2	1	B	1.00	1.14	0.892)	0.892)
TEG,sample 3	2	A	0.95	1.04	1.012)	0.962)
TEG,sample 4	2	B	1.01	1.14	0.942)	0.902)
TEG,sample 5	23)	B	0.95	1.08	0.862)	0.952)
Sigraflex®			0.87	1.39	0.82	1.10
Grafoil®			0.94	1.20	1.032)	1.212)

1) corrected for 96% carbon in the natural graphite
2) voltage scan rate 2 mV s^{-1} 3) 10% overoxidation

A slow cyclovoltammogram in 18 M H_2SO_4 for pristine graphite is in full agreement to that reported elsewhere.[10] Fig.2 shows the corresponding CV-curves for exfoliated samples. Besides the occurance of rather slim peaks, the features of these curves are quite in analogy to the pristine graphite curve. An evaluation of these measurements in terms of current efficiency $\alpha = Q_{cath}/Q_{anod}$ and mass utilization $\mu = Q_{cath}/Q_{theor}$ is given in Table 1. Surprisingly α is 95-100% in all cases, independent of pristine graphite or TEG-samples. μ lies between 94 and 114%, and again no significant difference is found. It is only for the commercial products, that α is somewhat lower and μ even higher. The quantitative reversibility (α=1) of nontreated pristine graphite is only reproduced by the gradually heated TEG-samples (B), but not by (A). Thus the C_xOH, generated according to equation 3, is not reflected in the CV-behaviour.

CV-curves in 10 M H_2SO_4 are shown in Fig.3. The begin of the anodic intercalation is shifted from U_s= 200 mV to 740 mV. A linear positive shift of the intercalation potential with decreasing molar acid concentration is well known.[12] The first stage peak merges into the overvoltage current rise. Thus only stage 2 compounds can be obtained. The curves for TEG are much more structurized than the one for pristine graphite. α and μ evaluation is included in Table 1. Both are lower in comparison to 18 M H_2SO_4, as expected.

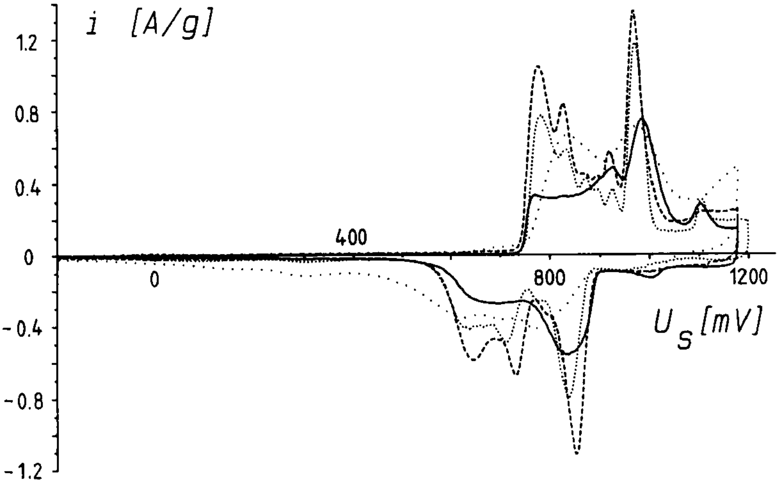


FIGURE 3 CV in 10 M H_2SO_4, v_s= 1 mV s^{-1}, 3rd cycle with "Großflocke" (———), TEG, sample 1 (·········) and sample 5 (– – – –), and Sigraflex (·····).

The broad potential region shown in Fig.3, where no intercalation occurs, seems to be a suitable basis to study surface redox processes by CV. Fig.4 displays some results at a voltage scan rate of 20 mV s^{-1}. In general, capacitive currents are observed, which are superimposed by a reversible redox peak at about U_s= 0 V, cf.[13] This is the redox potential of quinone/hydroquinone moieties. The currents are high in case of TEG, sample 3, and of Sigraflex®, but much lower for pristine graphite and for other TEG probes with a low degree of expansion. It was found, that the peak currents increase according to $i_p \sim v_s^{\nu}$, where ν was in the range of ν= 0.5...1.0. The peak voltages do not coincide, as it would be expected for surface bound redox processes. Integration of the curves yields Q in the potential interval ΔU= 0.9 V. Evaluation of capacity C according to dQ/dΔU leads to 3.1 and 6.1 F g^{-1} for the high currents, but only 0.2-0.4 F g^{-1} for the others. From the latter value, a specific area of 1-2 m^2 g^{-1} (with 20 μF cm^{-2}) can be derived.

CONCLUSIONS

The higher values must be attributed to redoxactive surface groups generated in the course of the exfoliation process. They are located at the rims of the edge planes. They are not identical with the OH groups according to

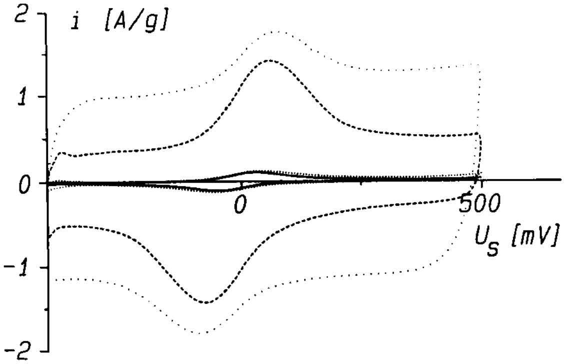


FIGURE 4 CV in 10 M H_2SO_4, v_S= 200 mV s^{-1}, 6th cycle after formation with 3 cycles as shown in Fig. 3; "Großflocke" (———), TEG, sample 1(·········) and sample 5(– – – –), and Sigraflex(······).

equation (3), for those are not redox active in the given potential region. Possibly, a selective high-temperature oxidation at the rims of the lamella occurs under the influence of SO_3:

$$C_x + SO_3 + H_2O \longrightarrow C_x(OH)_2 + SO_2 \qquad (4)$$

Also a total oxidation to CO_2 is discussed in the literature.[14]

No change of the GIC-capacity is to be expected. Lamella of 1000 graphene layers remain integer. If the freshly generated ab surfaces have any effect, this must be within only 0.1%. For battery application, this is far from any practical importance.

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