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ELECTROCHEMICAL INTERCALATION AND ELECTRICAL CONDUCTIVITY OF GRAPHITE FIBERS

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16. Abstract

Lamellar compounds of graphite fibers have been prepared by electrochemical intercalation. The dependence of the electrical resistance on the intercalate concentration was determined by a quasi simultaneous method. A factor 30 decrease of the relative fiber resistance was obtained with fluorosulfuric acid.

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ELECTROCHEMICAL INTERCALATION AND ELECTRICAL CONDUCTIVITY OF GRAPHITE FIBERS

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Introduction

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Through the investigations of Ruedorff (1) and Ubbelohde (2-5) we know that the electrical conductivity of lamellar graphite compounds is greater than that of graphite. Vogel (6) found in the treatment of graphite fibers with red, fuming HNO_3 a reduction of the specific resistance of 7.5×10^{-4} Ω cm to 7×10^{-5} Ω cm, therefore by a factor 10.

This article reports on the electrochemical interaction of graphite fibers with very high modulus of elasticity in strong acids; here the relation between the degree of intercalation and the electrical conductvity is of particular interest.

The authors used the commercial graphite fibers Celion GY 70 of the company Celanese, USA (modulus of elasticity = 5.17×10^{11} Nm^{-2}) and Thornel[R] 50 of Union Carbide, USA (modulus of elasticity = 4×10^{11} Nm^{-2}).

The incorporation and subsequent measurement of resistance took place at room temperature on individual fibers 3 to 4 cm long; to this end these were in u-shaped contact on Cu bars and the contact points were subsequently gold-plated by galvanic means.

To adjust certain degrees of intercalation the fibers were oxidized anodically with 2 μA direct current, while Pt was used as counterelectrode.

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By this method as we know it is possible to prepare even very small degrees of incorporation (3,7).

The intercalation was interrupted periodically (alternating switch) and the resistance of the fiber was determined practically free from debt time through the drop in voltage for 10 μA direct current.

Test measurements showed that with this method the flow of current through the electrolyte is negligible so that the resistance of the fibers could be determined directly in the electrolyte solution.

Raster electron microscopy photographs showed that the fibers used were not at all round or uniform in cross-section; therefore the specific electrical resistance was not indicated[1].

The measurement results were represented by the dependence of the relative fiber resistance R/Ro on the mass standardized charge quantity Q standardized. Thus it is assured that a certain Q standardized gives for all studied fibers a certain degree of intercalation (Figures 1 and 2). The weights of the individual fibers could not be determined with sufficient precision, so that the standardization was carried out to a factor proportional to weight l^2/R_o (l = fiber length, Ro = resistance of the initial fiber.

Results and Discussion

Figure 1 shows a variation of R/Ro as a function of Q standardized for Celion GY 70 in about 96 percent H2SO4.

[1] For a typical cross-section of 7×10^{7} cm^2 for Celion GY 70 the specific resistance is calculated at about 7×10^{-4} Ω cm.

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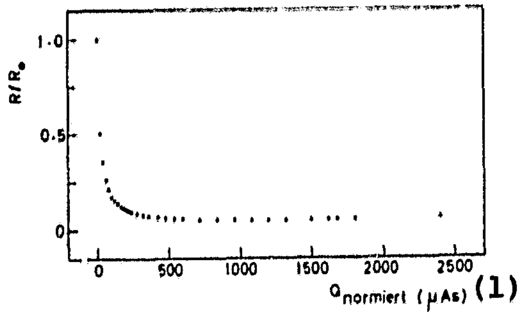

Figure 1: Relative resistance of Celion GY 70 as a function of Q standardized.

Key: (1) Q standardized.

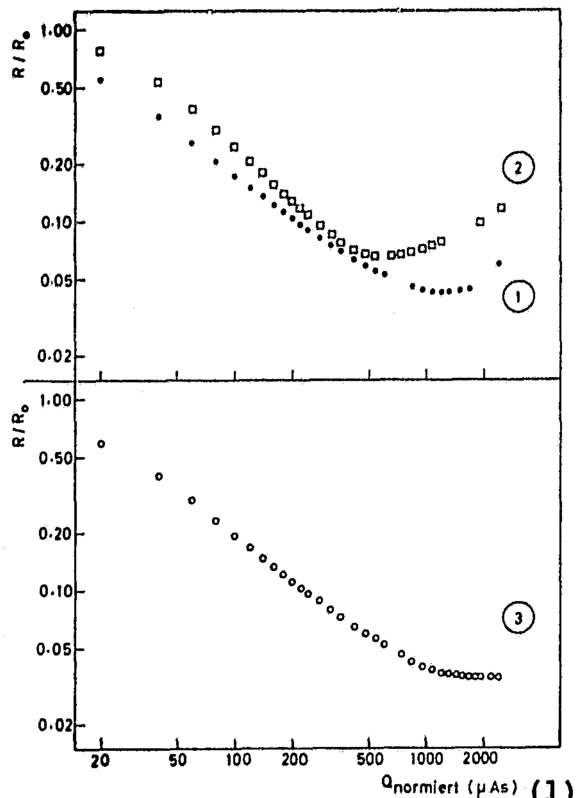

Figure 2: Relative resistance of Celion GY 70 as a function of (the double logarithmic) degree of intercalation; electrolyte = (1) about 96 percent H_2SO_4, (2) 70 percent H_2SO_4, (3) 100 percent FSO_3H. Key: (1) Q standardized.

The very sharp drop of R/R_o for a low degree of incorporation is characteristic. An estimate shows that for about 96 percent H_2SO_4 and 100 percent FSO_3H (Figure 2, curve 3) a reduction of R/R_o to half of the initial value is achieved already for a ratio of the C atoms/intercalate

= 1500 to 1; this corresponds to an incorporation density of about 7 by 10power19 anions per cm3. There is no linear relation between anion density and the relative resistance R/Ro, rather R/Ro tends with increasing degree of incorporation to a saturation value.

Figure 2 shows R/Ro plotted in double logarithmic representation against Q standardized.

In this representation we obtain a case of nondehydrated acid, a clear minimum; the latter for about 96 percent H2SO4 lies in the range of C24 + HSO4= (=first stage) and for 70 percent H2SO4 for a lower degree of incorporation. This may be explained by the fact that intercalation takes place initially and after passing through a minimum the formation of "graphite oxide" begins. This minimum does not appear for 100 percent FSO3H; here there is no water needed to form the "graphite oxide". With decreasing acid concentration this minimum is observed earlier (Figure 2, curve 2) since the hydrolysis of the graphite salt takes place earlier according to

$$C_n + HSO_4^- + H_2O = C_nOH + H_2SO_4.$$

The greatest variation of resistance was found for dehydrated FSO3H as electrolyte; here a ratio was obtained Ro/Rmin = 30.

The table shows further results:

Elektrolyt (1)		R_0/R_{min}
H_2SO_4	*ca.* 100-proz. (2)	23
H_2SO_4	*ca.* 96-proz.	23–25
H_2SO_4	90-proz.	23
H_2SO_4	80-proz.	16
H_2SO_4	70-proz.	15
$HClO_4$	70-proz.	13
FSO_3H	100-proz.	30–33
HNO_3	100-proz.	19
CF_3CO_2H	100-proz.	20

Key: (1) Electrolyte; (2) percent.

From the table it may be seen that in the case of sulfuric acid in a concentration range of 100 to 90 percent acid practically the same value is obtained for Ro/Rmin.

For Thornel^{R}50 fibers similar values were found for Ro/Rmin, of course the specific resistance of the initial fibers is higher by a factor of about 3 than for Celion GY 70.

For all intercalation tests it was observed that the mechanical properties and the diameter of the fibers vary only a little. Since /739 the density of Celion GY 70 is about 1.6 gcm^{-3} (graphite 2.25 gcm^{-3}), it may be assumed that internal cavities are filled predominantly by the expansion of the layers.

If organic electrolyte solutions are used for the electrochemical oxidation (incorporation of anions) or reduction (incorporation of cations) considerable decreases of resistance are also found. A forthcoming report will be published on this area and on the dependence of incorporation on the modulus of elasticity.

We thank Dr. A. Lerf, of the Central Institute of Low Temperature Research of the Bavarian Academy of Sciences in Garching for many stimulating discussions.

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