TECHNICAL NOTE

# Electrochemical oxidation of the surface of graphite fibres

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The influence of surface-oxide layers on metallic anodes in electrochemical reactions is well-recognized [1]. Comparatively little work has appeared, however, on the nature and role of surface oxides of carbon. These oxides may be no less important in governing the course of anodic reactions. For example, it is known that surface oxides of carbon affect wettability and the adsorption of inorganic and organic substrates [2–4].

For those using carbon electrodes in analytical or synthetic work the following communication should be of considerable interest. Little cognizance has been given to surface oxides present on anodized carbon electrodes.

Chemical oxidation of various carbons may be carried out by air or oxygen, or by mixing the carbon with aqueous solutions of sodium hypochlorite, permanganate, or persulfate [2–4]. Four oxide species have been identified: strongly acidic carboxylic acid, weakly acidic carboxylic acid, phenolic hydroxyl, and carbonyl. Two structures, an open form **1** and a lactone form **2** have been suggested. (See next column.)

The electrochemical oxidation of graphite has been examined by a number of workers [5–8] since 1881 when Bartoli and Papasogli reported the formation of mellitic and pyromellitic acids on oxidation in aqueous alkali. Apparently the first step in the oxidation is the generation of an interlaminar compound $c_n^+A^-$ ($n = 24, 32, 48, 64, 72$; $A^-$ corresponds to the anion of the supporting electrolyte). In concentrated acids



**1** Open form      **2** Lactone form
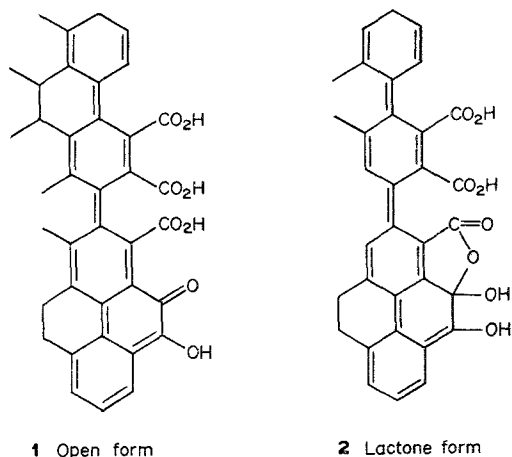
these species are fairly stable [9, 10] but in dilute aqueous solution hydrolysis occurs [11].

$$C_n + H_2SO_4 \rightarrow C_n^+HSO_4^- + H^+ + e$$

$$C_n^+HSO_4^- + H_2O \rightarrow C_nOH + H_2SO_4$$
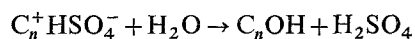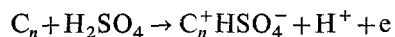
The hydroxylated species is then readily oxidized to other functions including carbonyl and carboxyl.

Recently Dietz and Peover [12] attempted to determine the surface area and detect surface groups on carbon fibres via electrochemical techniques. They found that the interlaminar shear strength of the corresponding epoxy resin composite could be correlated with the area wetted by electrolyte.

We were interested in anodically modifying the surface of Thorne 1-50$^R$ graphite fibre (Union Carbide Corporation) for use in the manufacture of carbon fibre-epoxy resin composites. We believed that the oxides should form chemical bonds to epoxy resins, leading to greatly streng-

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Table 1. Electrochemical oxidation of graphite fibre in 15% sulfuric acid

| Sample weight g | Potential V versus SCE | mEq NaOH/100 g | mEq NaHCO$_3$/100 g | Coulombs passed/100 g ($\times 10^5$) |
|---|---|---|---|---|
| Blank | — | 9, 11 | 0, 1 | 0·00 |
| 6·4 | 1·95–2·1 | 24 | 9 | 0·56 |
| 0·208 | 3·50* | 34 | — | 0·55 |
| 0·210 | 2·50* | 42 | — | 0·90 |
| 0·171 | 1·75–1·88 | 45 | — | 0·98 |
| 5·4 | 2·0–2·4 | 52 | 18 | 1·3 |
| 5·4 | 2·0–2·5 | 57 | 18 | 1·3 |
| 5·9 | 1·95–2·5 | 82 | 40 | 2·4 |

* Controlled potential oxidations.

thened materials. Samples of fibre (0·2–6·5 g) were wound on a polyethylene holder or suspended in solution (15% aqueous sulphuric acid). A large carbon rod served as cathode, and the solution was magnetically stirred. No cell divider was used. An aqueous SCE reference electrode was positioned in the solution near the graphite fibre anode. Most of the constant-current electrolyses were conducted at 20°C using a Harrison Laboratories Model 881A D.C. power supply. An Electrometer (Keithley Instruments, Model 610A) indicated the anode potential. Several controlled potential electrolyses were performed with a Wenking Potentiostat (Model 61 RS). After electrolysis the fibre* was washed well with distilled water† and dried *in vacuo* over P$_2$O$_5$ at 100°C, 0·1 mm Hg. Samples of this material were titrated according to the literature procedure of Boehm *et al.* [2]: the surface concentrations of carboxylic acid and phenol groups were determined with aqueous NaOH solution and that of the more strongly acidic carboxylic acid groups with aqueous NaHCO$_3$ solution. The results are shown in Table 1 and Fig. 1.

The slope for the NaOH curve is $3·60 \times 10^{-4}$ and that for NaHCO$_3$ is $1·66 \times 10^{-4}$ mEq/C. The ratio of the two slopes is 2·17 which is approximately the titration ratio obtained by Boehm *et al.* [2] for chemical oxidation of a variety of carbons in aqueous solution. Thus

* A small portion of the fibre, attached by means of an alligator clip, made electrical contact outside of the solution and was discarded.
† Microanalysis showed no detectable sulfate was present.

the nature of the electrochemically generated surface oxide appears to be quite similar to that obtained chemically in aqueous solution.

Table 1 and Fig. 1 show that there is little or no effect of working potential on the surface-oxide products as determined by NaOH and NaHCO$_3$ titrations. Widely differing chemical oxidants produce essentially similar surface oxides [2]. Once oxidation has begun, both chemical and electrochemical methods proceed through apparently similar sequences of C−C bond-breaking, C=C hydroxylation, C−OH oxidation, etc., to produce the same oxide surface.

In a further experiment, graphite oxidized anodically to the extent of $1·3 \times 10^5$ C/100 g was cathodically reduced ($0·34 \times 10^5$ C/100 g). The product showed titrations of 25 mEq/100 g for NaOH and 10 mEq/100 g for NaHCO$_3$. Thus the titratable surface oxides were removed by about a factor of 2 in a reduction which was carried out to the extent of about 1/4 of oxida-
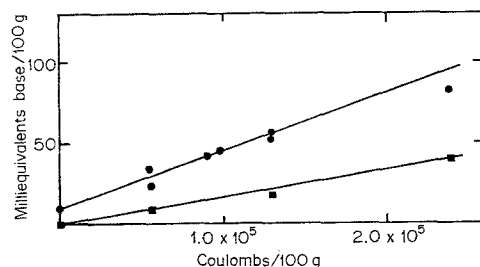


Fig. 1. Electrochemical oxidation of graphite in 15% H$_2$SO$_4$. Titrations with NaOH ●, and NaHCO$_3$ ■ solutions.

tion. Boehm *et al.* [2] have explained their chemical reduction results in terms of reduction of surface lactone or lactol groups, and a similar explanation appears to be justified for the electrochemical observations.

It is pertinent to note that controlled potential oxidation of graphite proceeded with a decaying current, indicative of passivation and formation of carbon oxide surface. Using the electrochemical method, the oxide surface may be reproducibly and conveniently generated. Recent patents [13, 14] indicate that electrochemical oxidation of graphite fibres may be a useful method of improving adhesion in composite materials between the fibres and the epoxy resin.

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