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Chemical modification of carbon fibres by esterification — optimization of fibre pretreatment

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Electrochemically oxidized PAN-based carbon fibres were modified by attachment of an *m*-dinitrobenzene group. Chemical modification was performed by esterification of the –OH groups of the oxidized carbon surface with 3,5-dinitrobenzoyl chloride. The higher modification extent was achieved in the case of d.c. oxidized carbon fibres, which bear a large number of –OH groups. The attachment of the dinitrobenzene species was supported by cyclic voltammetry carried out on the modified carbon fibre electrodes in aqueous solutions. The quantity of attached *m*-dinitrobenzene groups was determined polarographically, after hydrolysis of the esteric bonds; it corresponds to a charge density of ca $0.2\,\mathrm{kAh\,kg^{-1}}$ carbon fibres, which is of the order of magnitude of battery electrodes.

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1. Introduction

Chemical modification of carbon electrodes makes use of oxygen-containing functional groups on carbon ('surface oxides'), allowing a covalent linkage between carbon and specifically active 'modifiers'. Effective modification requires a high concentration of surface oxides. Moreover, it should be possible to 'custom-tailor' the composition of surface oxides, above all the ratio between –COOH and $\geqslant$COH groups. For chemical modification by esterification with carbonic acid chlorides only $\geqslant$COH groups are useful and hence their concentration should be high, whereas –COOH groups are not only useless but a waste of surface area in this case.

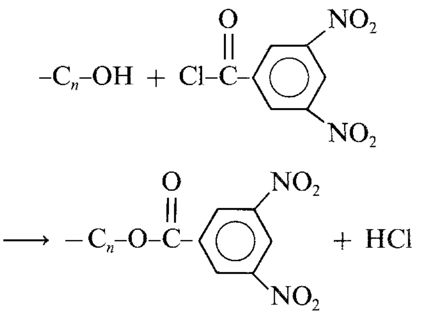
There are three main procedures for surface functionalization of carbons: chemical, thermal and electrochemical oxidation. Usually, electrochemical oxidation is much more effective than the others and, therefore, we concentrate on electrochemical procedures.

It has been shown in a previous study [1] that high current density anodic oxidation of PAN-based graphite carbon fibres in aqueous electrolytes leads to the formation of a large number of surface functional groups (such as phenolic –OH and –COOH groups) with cation-exchanging properties. Carbon fibre-supported noble metal catalysts can be prepared by exchange of the H^+ ions of these acidic functional groups with the cations of a noble metal salt, followed by reduction of the ions to the noble metal.

The large amount of surface functional groups on anodically oxidized carbon surfaces also enables the preparation of chemically modified electrodes. A general method for modification of –OH groups is the Williamson reaction: the hydrogen ions of these groups are displaced by Na^+ ions; the sodium compounds are then allowed to react with organic chloro-compounds in methanolic solutions [2, 3]

$$-C_n\text{-ONa} + \text{ClR} \longrightarrow -C_n\text{-OR} + \text{NaCl}$$

The present work makes use of the carbon surface functional groups for the preparation of chemically modified electrodes bearing the *m*-dinitrobenzene species (*m*-DNB group). The attachment of the *m*-dinitrobenzene species on the oxidized carbon fibres is achieved through the esterification reaction between the –OH groups of the carbon surface and 3,5-dinitrobenzoyl chloride



By combination of esterification and ion exchange even a discrimination between the –OH and the –COOH groups of the carbon surface is possible, since both kinds of groups participate in the cation exchange, while only the –OH groups react with 3,5-dinitrobenzoyl chloride.

Apart from the considerable interest of this reaction for the characterization of oxidized carbon surfaces

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there may also be some practical application: nitro-functionalization of highly oxidized high surface area carbon fibres can also be used for the immobilization of nitro-compound depolarizers in galvanic cells [4, 5].

The utilization of electrode surface functionalities for the attachment of electroactive moieties as modifiers or catalysers has been a subject of extended research in recent years [6–8].

2. Experimental details

Carbon fibre bundles (Celion GY 70, Celanese, USA) were pretreated electrochemically by two different procedures: (a) galvanostatic d.c. oxidation in 1 N Na_2SO_4 solution (optimum conditions: 12 min, 10 mA mg^{-1} C); (b) potentiostatic double pulse oxidation in 1 N Na_2SO_4 solution (optimized conditions: (1) potential range from +2.3 V to −0.3 V vs SCE; (2) oxidative pulse six times longer than the reductive pulse; (3) double pulse application time 6 min; (4) frequency ca 12 Hz).

For esterification with 3,5-dinitrobenzoyl chloride the oxidized fibres were washed with distilled water, vacuum dried and subsequently allowed to stand for 24 h in 0.5 M solution of 3,5-dinitrobenzoyl chloride in CCl_4. Adherent 3,5-dinitrobenzoyl chloride was removed by washing for about 10 h in CCl_4. The fibres were then again vacuum dried.

3,5-dinitrobenzoyl chloride (purum, Fluka) was recrystallized from carbon tetrachloride solutions.

Cyclic voltammetry was carried out using a conventional set-up. Repetitive pulse oxidation was controlled by a Bank double pulse generator DPC 72; pulse currents were recorded with a Biomation Model 805 waveform recorder.

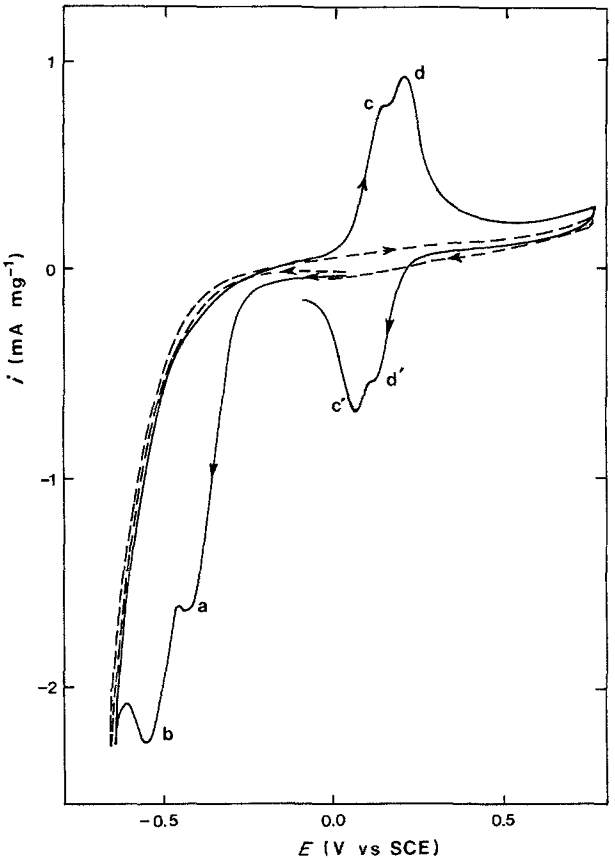
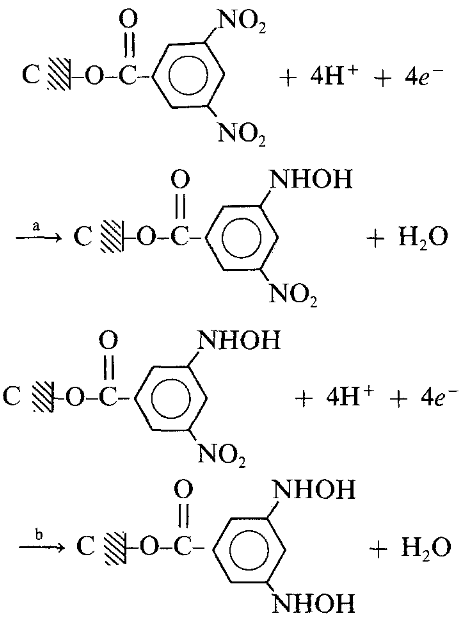


Fig. 1. Cyclic voltammograms (v = 20 mV s^{-1}, pH = 4) of pulse-oxidized carbon fibres modified with the *m*-DNB group. Dashed line: pulse-oxidized but non-modified fibres under the same conditions.

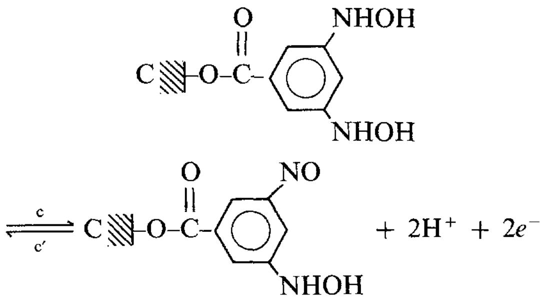
3. Results and discussion

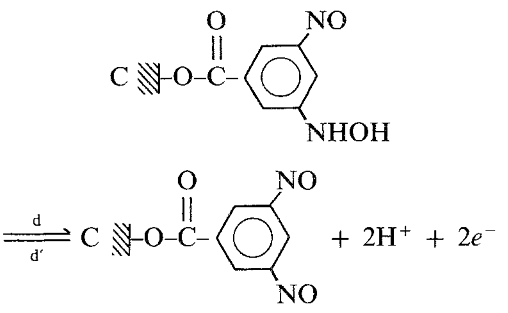
Figure 1 shows the cyclic voltammogram (in pH 4 aqueous solution) of carbon fibres modified with the *m*-DNB group, preoxidized by potentiostatic double pulse application. In the same figure (dashed line) the cyclic voltammogram of pulse oxidized non-modified fibres is presented.

The voltammograms of Fig. 1 were started from 0 V vs SCE in the cathodic direction. In the case of non-modified pulse oxidized fibres, the only reductive reaction that takes place begins at ca −0.5 V vs SCE and is attributed to the reduction of carbon surface oxides [1]. In the reverse sweep non-oxidative reaction is observed up to +0.7 V vs SCE. In the case of pulse oxidized fibres modified with the *m*-DNB group, two well-defined reduction waves (a and b) appear in the cathodic sweep; these are attributed to the successive reduction of the two nitro-groups of the attached *m*-DNB species to hydroxylamino-groups [9]:



In the reverse scan two waves (c and d) also appear, which correspond to the oxidation of the two hydroxylamino-groups to nitroso-groups. These two waves are reversible, as they result from the appearance of the peaks c′ and d′ during the second cathodic sweep; they are attributed to the rereduction of the nitroso- to hydroxylamino-groups





The presence of peaks a, b, c and d provides evidence that a significant quantity of the dinitrobenzene species has been attached to the carbon fibre electrode. The corresponding peak currents depend linearly on the potential scan rate, as is expected for species immobilized on the electrode surface [10]. The charge under the peaks (a + b) is almost twice that under the peaks (c + d) and certainly supports the reaction scheme presented above.

Peaks a and b disappear after a few successive scans, because the conversion of the nitro-groups to hydroxylamino-groups has meanwhile been accomplished. In contrast, peaks c, d, c′ and d′ are still present and increase in height until they level off to a limiting value. The shape of these latter peaks remains unaffected over numerous successive cycles. This fact indicates that stable attachment of the *m*-DNB group has been achieved by esterification.

When galvanostatic d.c. oxidation is employed for the pretreatment of the fibres instead of double pulse application, waves a and b cannot be discerned because they are superimposed by the reduction current of the 'graphitic oxides'. The oxides formed by galvanostatic d.c. oxidation are situated, not only on the surface, but also in the 'bulk' of the fibres. 'Bulk oxides' are reduced at more positive potentials than surface oxides [1, 11]. They are a by-product of d.c. surface oxidation of graphitic materials in acidic as well as in neutral aqueous electrolytes, where the surface of the anode becomes acidic because of the electrolysis of water. During d.c. oxidation the ionic intercalation compounds which are initially formed produce bulk oxides by hydrolysis, while during the double pulse application the formation of bulk oxides is significantly retarded.

The reversible pairs of peaks c, c′ and d, d′ are observed in the same potential region, independently of the oxidative procedure employed. However, it must be pointed out that these peaks are significantly higher when d.c. oxidized fibres are used.

Figure 2 shows the pairs of peaks c, c′ and d, d′ for modified pulse oxidized (curve 1) and d.c. oxidized (curve 2) fibres, respectively. The area under these peaks provides a relative measure of the extent of modification and, consequently, of the number of effective –OH groups on the oxidized graphitic substrate.

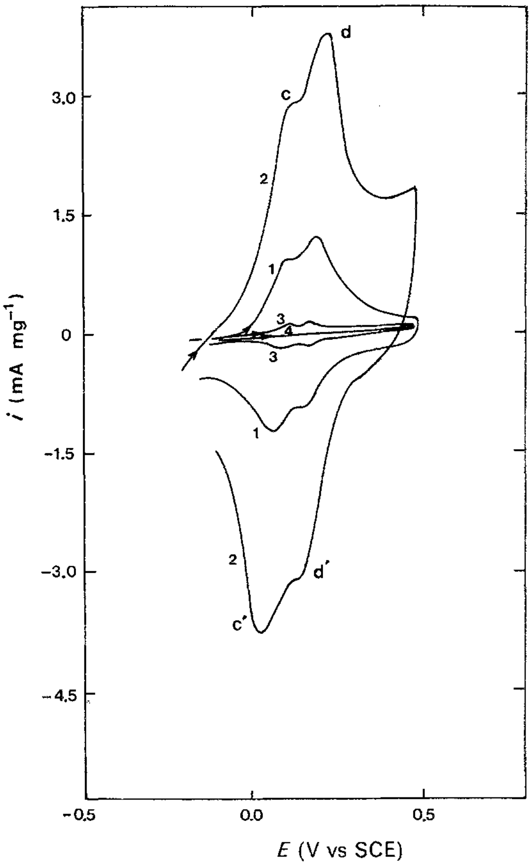


Fig. 2. Cyclic voltammograms ($v = 20\,\mathrm{mV\,s^{-1}}$, pH = 4) of the hydroxylamino-nitroso-groups redox reactions on carbon fibres modified with the *m*-DNB species, pretreated by: (1) double pulse; (2) d.c.; (3) chemical; and (4) thermal oxidation.

In order to evaluate the efficiency of electrochemical oxidation, referring to the creation of functional –OH groups, in comparison with classic oxidation procedures, esterification with 3,5-dinitrobenzoyl chloride was also carried out on chemically and thermally oxidized fibres. Chemical oxidation was carried out by treating the fibres in a solution of 0.2 M $KMnO_4$ in 2 M H_2SO_4 for 0.5 h at room temperature [5]. Thermal oxidation was achieved by heating the fibres at 150° C for 40 h in the presence of water vapour [12, 13].

In the case of chemically oxidized carbon fibres, the esterification results in a slightly enhanced modification, as seen from the peaks that can just be discerned in the corresponding cyclic voltammogram (Fig. 2, curve 3).

In the case of thermally oxidized carbon fibres, the esterification procedure does not result in modification of the fibres as is obvious from the absence of any peaks in the corresponding cyclic voltammogram (Fig. 2, curve 4). This behaviour indicates that thermal oxidation does not produce –OH groups on the graphitic substrate, in accordance with previous results which showed the presence of an excess of carboxylic groups on such oxidized carbon fibres [12, 13].

The results presented in Fig. 2 suggest that the most appropriate method for creating functional –OH groups on the graphitic substrate is the electrochemical oxidation of the fibres as described in the present study. This method results in an extremely high functionalization of the carbon material extended in three dimensions due to the microporous character of the PAN-based fibres.

Comparison of the two electrochemical procedures employed, i.e. pulse and d.c. oxidation, favours the latter as the most advantageous for pronounced modification by esterification.

The number of attached -NO_2 groups g^{-1} of carbon fibres was estimated by means of hydrolysis of the esteric bonds of the modified fibres after heating them in a 2 M NaOH solution for 1 h and subsequent polarographic determination of the quantity of the nitrobenzoic salt formed. It was found that ca 2×10^{-3} mol -NO_2 groups are present g^{-1} of d.c. oxidized fibres and ca 1×10^{-3} mol g^{-1} of pulse oxidized fibres.

The quantity of 2×10^{-3} mol -NO_2 groups corresponds to 8×10^{-3} Faradays, since 4 electrons are involved in the complete reduction of each -NO_2 group. This value corresponds to a charge density of ca 0.2 kAh kg^{-1} carbon fibres, which is of the order of magnitude for electrodes commonly used in batteries.

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