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Electrochemical oxidation of carbon fibres in aqueous solutions and analysis of the surface oxides

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Carbon fibres with notably different surface oxides can be prepared by varying the electrochemical oxidation conditions. Through correlation of voltammetric analysis and mass spectroscopy, interpretation of the reduction peaks of the surface oxides on the basis of their potential and width is possible. Narrow voltammetric reduction peaks at strongly negative potential are indicative of the predominance of –COOH type groups, while wide peaks at more positive potential are indicative of the presence of an excess of $\geqslant$C–OH type groups. A quantitative determination of the surface acidic groups (–COOH and $\geqslant$C–OH) is achieved by combination of Ag^+ ion exchange and esterification of $\geqslant$C–OH groups with 3,5-dinitrobenzoyl chloride. All results are confirmed by the independent method of –COOH group determination via their electrocatalytic behaviour in the reduction of azobenzene in methanol. The amounts of the –COOH and $\geqslant$C–OH groups formed depend notably on the conditions of the electrochemical oxidation of the carbon fibres. The ratio between –COOH and $\geqslant$C–OH groups coincides in all cases with that obtained by the mass spectrosopic data.

1. Introduction

The anodic oxidation of graphitic materials in aqueous solutions creates surface oxides and also three-dimensional defect oxides, consisting mainly of carboxylic and phenolic groups [1–4]. The composition of these oxides can be controlled to some extent by proper choice of current and potential profiles and also by the electrolyte solution. Effects of pH, electrolyte composition and current density on the properties and composition of surface oxides on carbon fibres have been reported previously by several authors [5–11].

Based on electrochemical and microscopic data, a mechanistic concept of electrolyte effects on carbon fibre surface oxidation was presented in a preceeding paper [4].

There are many methods available which have already been successfully used for the analysis of surface oxides and also of three-dimensional oxides on black carbons. The classical chemical methods [1, 12] are mainly designed for the analysis of activated carbon blacks and require considerable amounts of sample material.

High-vacuum methods of surface analysis have the disadvantage that they examine what remains of an originally hydrated surface. ESCA, which has been most widely used [5–9], suffers from poor discrimination between different oxides and also from lack of penetration depth. Therefore, it is not really adequate for the analysis of highly oxidized and, usually, microporous carbon materials.

Electroanalytical methods are highly sensitive and compare well with high-vacuum techniques. They can be performed in various aqueous and non-aqueous media, but like ESCA, they are not sufficiently discriminative for the direct determination of the various carbon–oxygen and carbon–oxygen–hydrogen groups. The combination of electroanalytical techniques with previous chemical modification of oxides on carbon, however, is a way for the determination of 'surface oxides', showing the selectivity of the modification reaction together with the sensitivity of electroanalytical techniques. Voltammetric reduction of dinitrobenzene derivatives [13–15], electrochemical adsorption studies on oxidized and trimethylsilanized carbon [16, 17], voltammetric determination of metal ions bonded on acidic oxides by cation exchange [18–20] and electrocatalytic reactions on oxidized carbon surfaces [17, 21] are typical examples of this group of analytical procedures.

In this paper we illustrate routes to custom-tailored oxides on highly oriented PAN (polyacrylonitrile)-based carbon fibres by studying the effects of drastically different electrochemical oxidation procedures on the amount and ratio of the created –COOH and $\geqslant$C–OH groups.

The determination of the above groups is achieved by combination of mass spectroscopy and several analytical techniques of the type modification plus electroanalysis. It turns out that not only the total amount of these groups on the fibres, but also the dominance of either –COOH or $\geqslant$C–OH can be controlled by the conditions of anodic oxidation.

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2. Experimental details

The electrochemical oxidation of the fibres was achieved by three different methods

(a) Direct current oxidation (DC) in 0.5 M Na_2SO_4 and 0.01 M NaOH with $i_{ox} = 10\,mA\,mg^{-1}$ carbon and $t_{ox} = 12\,min$.

(b) Controlled-current double-pulse oxidation (CCP) in 0.5 M Na_2SO_4 and 1 M $NaClO_4$ with $i_{ox} = 10\,mA\,mg^{-1}$ carbon, $i_{red} = 5\,mA\,mg^{-1}$ carbon, $t_{ox} = 24\,min$, $t_{red} = 24\,min$, $t_{total} = 48\,min$.

(c) Controlled-potential double-pulse oxidation (CPP) in 0.5 M Na_2SO_4 and 1 M $NaClO_4$ with $E_{ox} = 2.3\,V$, $E_{red} = -0.3\,V$, $t_{ox} = 4.5\,min$, $t_{red} = 0.75\,min$, $t_{total} = 6\,min$ [18].

CO/CO_2 analysis was carried out by heating the samples (13° min^{-1}) in a quartz container inside the mass spectrometer (CH5 Varian MAT) from room temperature up to about 800° C. Below about 100° C the mass spectra are very much affected by liberation of adsorbed species which may not be regarded as thermal decomposition products. The CO^+/CO_2^+ ratio was calculated from total counts and not corrected for CO^+ being a CO_2^+ fragment.

Cation-exchange of the H^+ ions of the acidic –COOH and ⩾C–OH groups on the electrooxidized fibres by Ag^+ was achieved by dipping the fibres in aqueous $AgNO_3$ solutions and subsequent washing with water [18]. Esterification of the ⩾C–OH groups of the oxidized fibres with 3,5-dinitrobenzoylchloride was performed in CCl_4 solutions [15]. The catalytic activity of the –COOH groups of the oxidized carbon fibres on the electroreduction of azobenzene was studied in methanolic solutions [21].

3. Results and discussion

As anodic oxidation of graphitic materials, even in dilute acidic solutions, yields intercalation compounds as by-products [18, 22], this study was limited to neutral and alkaline electrolytes. Nevertheless, some intercalation compounds are found after direct-current oxidation in neutral electrolytes because of the considerable acidification of the diffusion layer of the anode. Using alternating current oxidation with current reversal, intercalation can be almost completely avoided [15, 18, 19].

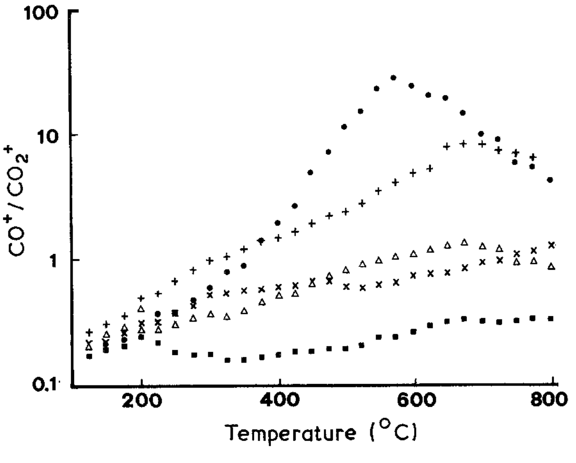


Fig. 1. CO^+/CO_2^+ ratio of thermal decomposition of oxidized carbon fibres (Celion GY 70) in a mass spectrometer. Oxidation procedure: (●) DC in 0.5 M Na_2SO_4 (+) CCP in 1 M $NaClO_4$ (△) DC in 0.01 M NaOH (x) CCP in 0.5 M Na_2SO_4 (■) CPP in 0.5 M Na_2SO_4.

For a convenient determination of the kind and amount of oxidation products on carbon fibres, weighed samples were thermally decomposed, after washing and vacuum drying in a mass spectrometer. CO_2 was assumed to be liberated from –COOH groups and CO was attributed to the rest of the carbon–oxygen–hydrogen complexes which, for simplicity, will be referred to as 'OH-type'. In Fig. 1, the CO^+/CO_2^+ ratio is plotted against decomposition temperature of the samples.

The mass spectroscopic results, for the amounts of the –COOH and ⩾C–OH groups, roughly fit the data obtained from linear sweep voltammetry and other analytical techniques, as presented below.

In Fig. 2, the cathodic sweeps of the voltammograms of carbon fibres electrochemically oxidized by different procedures are given in 0.5 M H_2SO_4. As can be seen from the voltammetric analysis (Fig. 2 and Table 1), the total amount of oxides is comparable for the different oxidation procedures used. There are, however, considerable differences in their composition.

In Na_2SO_4 solutions, double-pulse oxidation procedures create much more –COOH and less –OH-type groups than direct-current oxidation. This is true for controlled current as well as for controlled potential double-pulse oxidation. This agrees with the concept that repeated oxidation–reduction cycles break more C–C bonds than constant current oxidation does, so creating terminal carbon atoms that can be transformed to –COOH groups. The slightly higher fraction of –COOH groups after CPP as compared to CCP is probably related to the much higher peak currents in CPP.

Direct-current oxidation in Na_2SO_4 solutions, in addition to surface and defect oxides, does also yield some graphite oxide which is formed by hydrolysis of sulphuric acid intercalation compounds. As graphite oxide is a strong oxidant, it can be easily distinguished from surface and defect oxides by its much more positive reduction potential (see Fig. 2, curve a).

The surface and defect oxides formed after direct current oxidation in dilute NaOH have properties very similar to those obtained by double-pulse oxidation in 0.5 M Na_2SO_4. This agrees with the shapes of their reduction voltammograms (Fig 2) and also with microscopic studies [4].

Comparing the voltammetric data (Fig. 2 and Table 1) of carbon fibres oxidized by different procedures with their mass spectrometric data (Fig. 1), there is an obvious correlation between the shapes of the voltammetric peaks, peak potentials and CO^+/CO_2^+ ratios, i.e. ratios between –OH-type and –COOH groups.

Narrow voltammetric reduction peaks at strongly

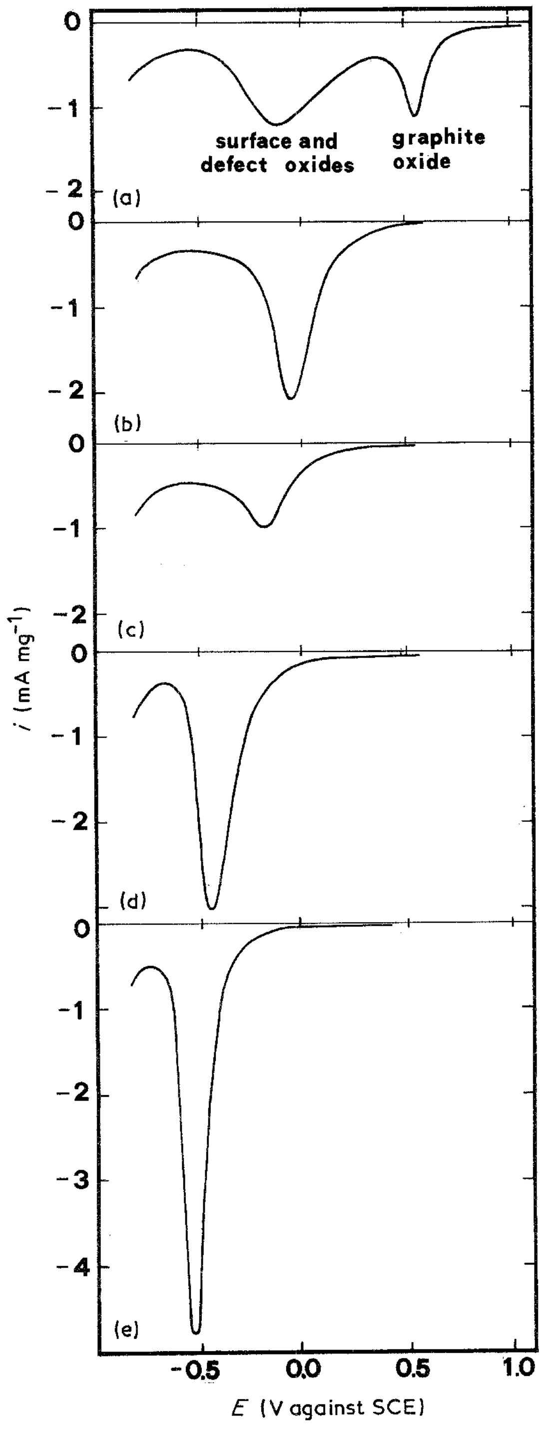


Fig. 2. Cathodic sweeps ($v = 1\,\mathrm{mV\,s^{-1}}$) of oxidized carbon fibres (Celion GY 70) in 0.05 M H_2SO_4. Oxidation procedure: (a) DC in 0.5 M Na_2SO_4 (b) CCP in 1 M $NaClO_4$ (c) DC in 0.01 M NaOH (d) CCP in 0.5 M Na_2SO_4 (e) CPP in 0.5 M Na_2SO_4.

negative potential are indicative of the predominance of –COOH type groups. The wider the reduction peaks and the more positive their reduction potential, the higher the fraction of –OH-type groups.

It must be pointed out that, even after the reduction of the surface and defect oxides, a strongly functionalized graphitic material is obtained. This was proved by the fact that the reduced material bears funtional groups which cause chemical reduction of Ag^+ ions to metallic silver. Further evidence for the existence of functional groups on the rereduced carbon material is provided by ESCA spectroscopy.

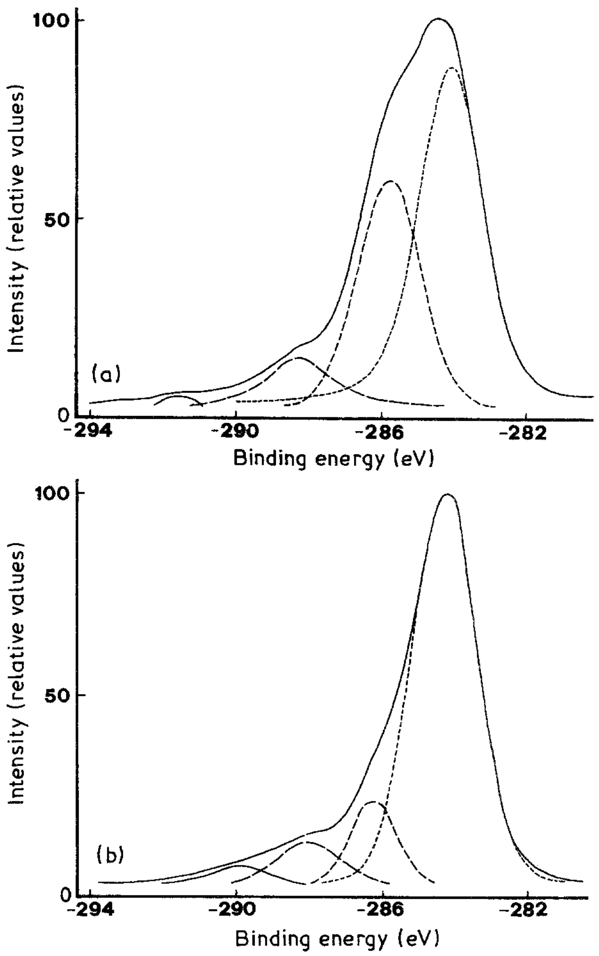


Fig. 3. C_{1s} ESCA spectra of carbon fibres (Graphil) after (a) galvanostatic oxidation in 0.5 M H_2SO_4 ($i = 10\,\mathrm{mA\,mg^{-1}}$ carbon, $t = 1$ min) and (b) after galvanostatic oxidation and rereduction in 0.5 M H_2SO_4 ($i = -10\,\mathrm{mA\,mg^{-1}}$ carbon, $t = 1$ min).

An example of ESCA spectra obtained with galvanostatically oxidized and with galvanostatically rereduced carbon fibres in 0.5 M H_2SO_4 is given in Fig. 3. The corresponding data are presented in Table 2.

It must be emphasized that electrochemical reduction of surface and defect oxides is a kinetically hindered and also a strongly pH-dependent process. Therefore, comparison of voltammograms is only useful under strictly standard conditions, the most important parameters being sweep rate and pH of the electrolyte. Increasing sweep rate broadens the peaks and shifts their potentials in the negative direction; increasing pH also shifts E_p to more negative potentials but in this case the peaks are more narrow.

Afterwards, the total amount of –COOH and $\geqslant$C–OH groups, as well as the partial quantities of these groups, on oxidized carbon fibres were determined by a combination of simple chemical and electrochemical reactions.

An established method for the determination of –OH-type surface groups on carbons is their chemical modification by esterification with 3,5-dinitrobenzoyl chloride, followed by voltammetric reduction of the nitro groups [15]. Carboxylic groups on carbons can be determined by means of their

Table 1. Voltammetric data of the reduction peak of surface and defect oxides on carbon fibres in 0.5 M H_2SO_4

Oxidation procedure	E_p (*mV against SCE*)	Q_{red} (*mA s mg*$^{-1}$ *carbon*)	*Peak shape h/w* (*mA mV*$^{-1}$ × 100)
DC 0.5 M Na_2SO_4	−120	410	0.2
CCP 1 M $NaClO_4$	−75	580	0.9
DC 0.01 M NaOH	−180	250	0.5
CCP 0.5 M Na_2SO_4	−350	700	1.8
CPP 0.5 M Na_2SO_4	−530	760	3.9

catalytic activity in the electrochemical reduction of azo compounds [21].

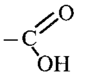
Because of their acidity, ⩾C–OH and –COOH groups on carbons show cation exchanger properties. We found that the cation exchange capacity, e.g. for Ag^+-cations, which can easily be measured by linear sweep voltammetry, corresponds to the total of –OH-type and –COOH-type groups determined by the two above-mentioned methods.

Regarding the sensitivity of electroanalytical methods, this opens the door to a relatively convenient and, because of the two independent routes for either ⩾C–OH or –COOH determination, also a very reliable analysis for surface groups in the submicromole range.

The surface groups on carbon fibres electrochemically oxidized by different procedures were determined by combination of Ag^+ ion exchange and esterification of ⩾C–OH groups with 3,5-dinitrobenzoyl chloride. All results were confirmed by the independent method of –COOH group determination via the electrocatalytic behaviour in the reduction of azobenzene in methanol.

Dealing with highly oxidized and hence microporous carbon samples there is a drawback with voltammetric methods, because of their poor ability to penetrate into the bulk of the carbon material. In the case of thin carbon fibres (about 8 μm) used in this study, bulk effects were not a serious complication. However, supplementary methods were also used for the determination of the amounts of acidic groups on the electrooxidized fibres, such as atomic adsorption spectroscopy for the ion-exchanged silver, d.c. polarography for the determination of ⩾C–OH groups esterified with 3,5-dinitrobenzoyl chloride and con-

Table 2. Data of the C_{1s} *ESCA spectra of Fig. 3*

Carbon function	*Binding energy* (*eV*)	*Intensity* (*relative values*)	
		before reduction	*after reduction*
⩾C–C⩽	−284.2	100	100
⩾C–OH	−285.7	55.4	21.4
>C=O	−288.0	17.6	10.7
 $-C(=O)OH$	−290 til −292	2.8	6.3

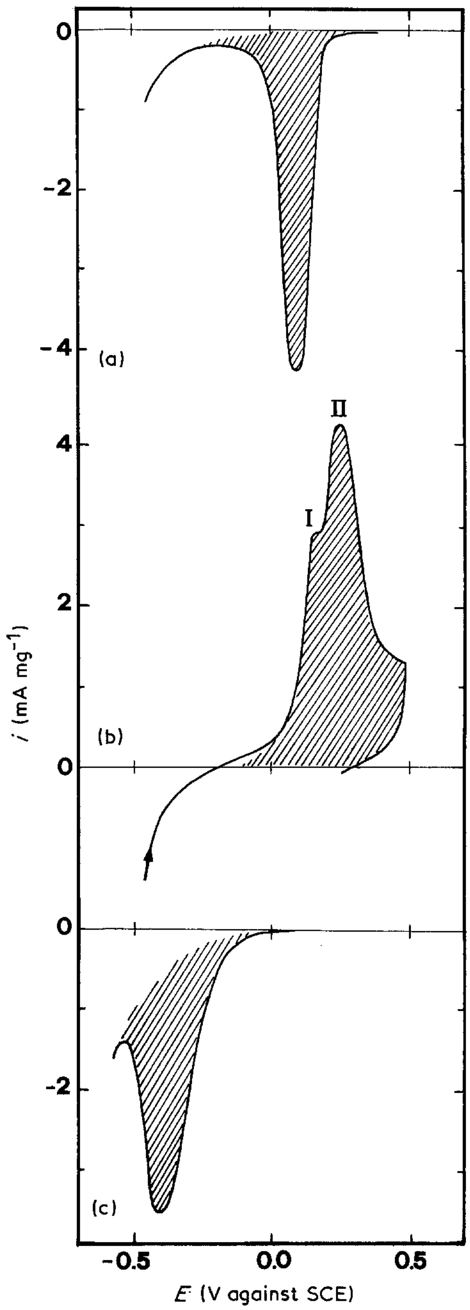


Fig. 4. Voltammograms (v = 5 mV s^{-1}) of (a) Ag^+-loaded carbon fibres in pH = 4 aqueous solution (b) of carbon fibres modified with the 3,5-dinitrobenzene group in pH = 4 aqueous solution and (c) of oxidized carbon fibres in the presence of azobenzene (c = 1.5 × 10^{-2} M) in methanolic (0.1 M $LiClO_4$) solution. Fibres oxidized by CCP in 0.5 M Na_2SO_4.

Table 3. Amounts of surface groups on carbon fibres (Celion GY 70) electrochemically oxidized by different procedures

Oxidation procedure	*Total amount of acidic groups ($meq\,g^{-1}$ carbon)*	*–COOH groups ($meq\,g^{-1}$ carbon)*	*⩾C–OH groups ($meq\,g^{-1}$ carbon)*
DC 0.5 M Na_2SO_4	0.6	-	0.6
DC 0.01 M NaOH	0.4	0.2	0.2
CCP 0.5 M Na_2SO_4	1.2	0.6	0.6
CCP 1 M $NaClO_4$	0.9	0.3	0.6
CPP 0.5 M Na_2SO_4	1.2	0.9	0.3
CPP 1 M $NaClO_4$	0.9	0.6	0.3

stant potential electrolysis for the estimation of –COOH groups which cause electrocatalysis of azobenzene reduction.

The cyclic voltammetric behaviour of carbon fibres electrooxidized by CCP in 0.5 M Na_2SO_4, is illustrated as an example in Fig. 4a, where these fibres have been ion-exchanged by Ag^+ ions, in Fig. 4b, where the ⩾C–OH groups of such oxidized fibres have been esterified by 3,5-dinitrobenzoyl chloride and in Fig. 4c, where the azobenzene reduction in methanol has been electrocatalysed by the –COOH groups of these fibres.

The amount of exchanged Ag^+, estimated from the area under the reduction peak of Ag^+ to metallic silver (hatched region in Fig. 4a), was found to be about 1.2 $meq\,g^{-1}$ carbon fibres. This quantity corresponds to the total of the cation-exchangeable groups (⩾C–OH and –COOH) on the CCP-oxidized carbon fibres. This result was verified by Ag determination through atomic adsorption spectroscopy.

In Fig. 4b, the cyclic voltammogram was recorded after the carbon fibres, oxidized and modified by the 3,5-dinitrobenzene species, had been held at –0.5 V vs SCE for 1 min in a pH = 4 aqueous solution. At this potential, both the attached $-NO_2$ groups are reduced to –NHOH groups. The peaks due to the reduction of the $-NO_2$ groups cannot be discerned because they are superimposed on the reduction current of the 'graphitic oxides'. In the reverse scan, two waves, I and II, appear, corresponding to the oxidation of the two –NHOH groups to –NO groups. From the total charge under the peaks I and II (hatched region in Fig. 4b), the amount of ⩾C–OH groups, which have reacted with 3,5-dinitrobenzoyl chloride was estimated to be about 0.6 $meq\,g^{-1}$ carbon fibres. This value is in satisfactory agreement with the result obtained by the polarographic determination of the quantity of the dinitrobenzoic salt formed after hydrolysis of the esteric bonds of the modified carbon fibres [15].

According to the above values for all the acidic and the ⩾C–OH groups, the amount of –COOH groups should be about 0.6 $meq\,g^{-1}$ fibres. The estimation of the –COOH groups can be alternatively verified by the electrochemical study of the reduction of azobenzene to hydrazobenzene on the CCP-oxidized carbon fibres in methanolic solution (Fig. 4c). The carboxylic groups of the oxidized carbon surface catalyse the electroreduction of azobenzene, so that the reduction peak appears at –0.4 V vs SCE, whereas the formal reduction potential of azobenzene on pristine carbon fibres is –1.1 V vs SCE. From the integration of the reduction peak (hatched region in Fig. 4c), the amount of –COOH groups present on the oxidized carbon surface was estimated to be indeed 0.6 $meq\,g^{-1}$ carbon fibres. This result was confirmed by means of electrolysis at –0.45 V vs SCE on large bundles of oxidized carbon fibres [21].

The total amount of acidic groups as well as the respective content of –COOH and ⩾C–OH groups estimated by the above-mentioned methods, for carbon fibres electrochemically oxidized by all the employed procedures, are summarized in Table 3.

The total amounts of acidic surface groups determined by the electrochemical and chemical reactions used in this study, are directly proportional to the charges under the reduction peaks of the surface oxides obtained in 0.5 M H_2SO_4 (Fig. 2 and Table 1).

The ratio between ⩾C–OH and –COOH groups coincides in all cases with that obtained by mass spectroscopy of the thermal decomposition products CO and CO_2.

4. Conclusion

It has been demonstrated that custom-tailored surface groups (–COOH and ⩾C–OH) on carbon fibres can be electrochemically obtained by choice of current profiles and electrolyte.

The total amount of –COOH and ⩾C–OH groups, as well as the partial quantities of these groups, can be determined by a combination of simple chemical and electrochemical reactions. For these determinations very small quantities of carbon fibre are required.

References

[1] H. P. Boehm, *Angew. Chem. Int. Ed. Engl.* **5** (1966) 533.

[2] J. P. Randin, in 'Encyclopedia of Electrochemistry of the Elements', Vol. 7 (edited by A. J. Bard), Marcel Dekker, New York (1976) p. 22.

[3] J. O. Besenhard and H. P. Fritz, *Angew. Chem., Int. Ed. Engl.* **22** (1983) 950.

[4] J. O. Besenhard, J. Jakob, U. Krebber, P. Möller, R. F. Sauter, A. Kurtze, N. Kanani, H. Meyer, J. K. H. Hörber and A. D. Jannakoudakis, *Z. Naturforsch.* **44b** (1989) 729.

[5] A. Proctor and P. M. A. Sherwood, *J. Electron. Spectrosc. Relat. Phenom.* **27** (1982) 39.

[6] *Idem*, *Surf. Interface Anal.* **4** (1982) 212.

[7] *Idem*, *Carbon* **21** (1983) 53.

[8] C. Kozlowski and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. I* **80** (1984) 2099.

[9] *Idem*, *ibid.* **81** (1985) 2745.

[10] E. Fitzer, H. Jäger, N. Popovska and F. von Sturm, *J. Appl. Electrochem.* **18** (1988) 178.

[11] S. Neffe, *Carbon* **25** (1987) 761.

[12] B. R. Puri, 'Chemistry and Physics of Carbon', Vol. 6, Marcel Dekker, New York (1970) p. 191.

[13] C. M. Elliott and R. W. Murray, *Anal. Chem.* **48** (1976) 1247.

[14] M. Fujihira and T. Osa, *Prog. Batteries Solar Cells* **2** (1979) 244.

[15] P. D. Jannakoudakis, A. D. Jannakoudakis, E. Theodoriou and J. O. Besenhard, *J. Appl. Electrochem.* **19** (1989) 341.

[16] E. Theodòridou, J. O. Besenhard and H. P. Fritz, *J. Electroanal. Chem.* **124** (1981) 87.

[17] E. Theodoridou and A. D. Jannakoudakis, *Z. Phys. Chem. N. F.* **132** (1982) 175.

[18] E. Theodoridou, A. D. Jannakoudakis, J. O. Besenhard and R. F. Sauter, *Synth. Metals* **14** (1986) 125.

[19] *Idem*, in Proceedings of the 4th International Carbon Conference, Baden-Baden 1986, p. 623.

[20] E. Theodoridou, A. D. Jannakoudakis, P. D. Jannakoudakis, J. O. Besenhard and A. Kurtze, in 'Carbon '88', (edited by B. McEnany and T. J. Mays), 1988, p. 537.

[21] A. D. Jannakoudakis and E. Theodoridou, *Z. Phys. Chem. N. F.* **136** (1983) 225.

[22] F. Beck and H. Krohn, *Synth. Metals* **14** (1986) 137.